A Suzuki Coupling Based Route to 2,2'-Bis(2-indenyl)biphenyl Derivatives

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Contents of the supporting information:

- ?? Experimental procedure for **19**.
- ?? Characterization of **27** (including ^{1}H-, ^{13}C-, DEPT, ^{1}H-^{1}H COSY, ^{1}H-^{13}C correlation spectra) and X-Ray data for $(\mathbf{27})_2ZrCl_2$.
- ?? NMR spectra of **41**, **44**, **35**, **46**, **45**, **36**, **47** and **48**

1-(2'-indanylidene)-2-indanone ***(19).***

To a slurry of 2,2'-dilithiobiphenyl bis TMEDA adduct (**16**) (27.0 g, 67.8 mmol) in diethyl ether (125mL), a solution of 2-indanone (17.9 g, 136 mmol) in diethyl ether (150 mL) was added at room temperature. A small exothermic effect was observed. After stirring overnight, the reaction mixture was poured in water (100 mL). The pH was adjusted to 4 by a solution of hydrochloric acid in water (5%). The organic phase was separated. The aqueous phase was extracted with dichloromethane (3 ? 100 mL). The combined organic phases were extracted with a saturated NaCl solution (3 ? 50 mL), and dried over $NaSO_4$. The drying agent was filtered off and the solvents were removed under reduced pressure, resulting in a waxy residue. Precipitation from CH_2Cl_2/ligroin gave pure **19** as a slightly yellow powder (7.70 g, 46%), mp 183-184°C (Lit. 178°C[1]).

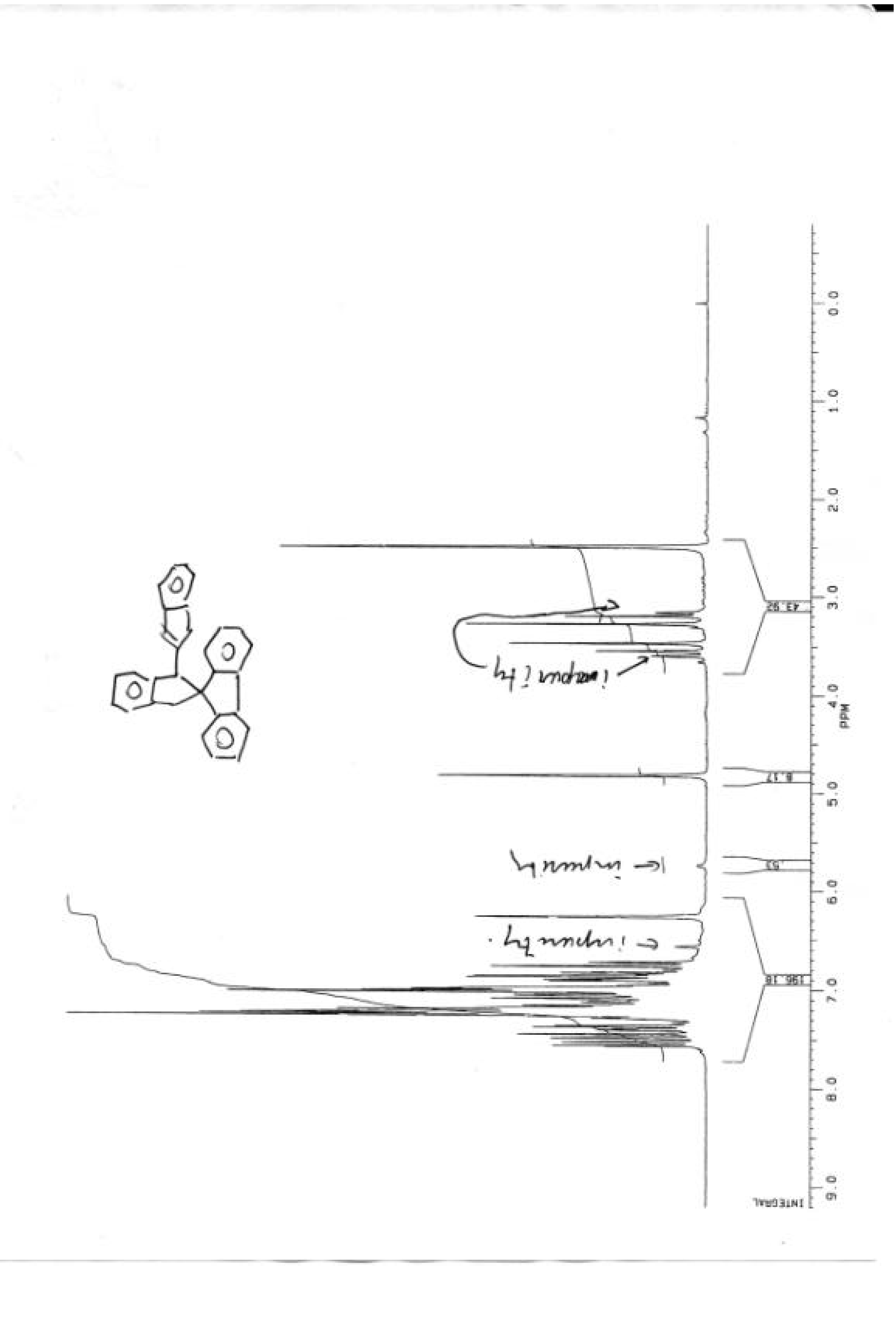
^{1}H-NMR ($CDCl_3$): d 7.56 (d, J = 6.20 Hz, 1H), 7.25 (m, 7H), 4.38 (tr, 2H), 4.14 (tr, 2H), 3.49 (s, 2H) ppm. ^{13}C-NMR ($CDCl_3$): d 204.7, 154.9, 141.9, 140.9, 140.0, 138.2, 130.4, 128.3, 128.0, 127.8, 127.5, 125.9, 125.4, 125.1, 124.3, 43.0, 42.0, 41.5 ppm. GC-MS: m/z: 246 (100%), 217 (89%), 202 (52%)

Characterization of ***27.***

GC-MS analysis of the reaction mixture indicates minor components having m/z = 406 (assigned to unconverted starting material **26**); m/z = 268 (assigned to the depicted 2-(2-indenyl)biphenyl (**28**) or an isomer thereof); m/z = 304 (assigned to the doubly reduced homo-coupling product of biphenyl) (**29**); m/z = 532 (attributed to **30** or an isomer thereof).

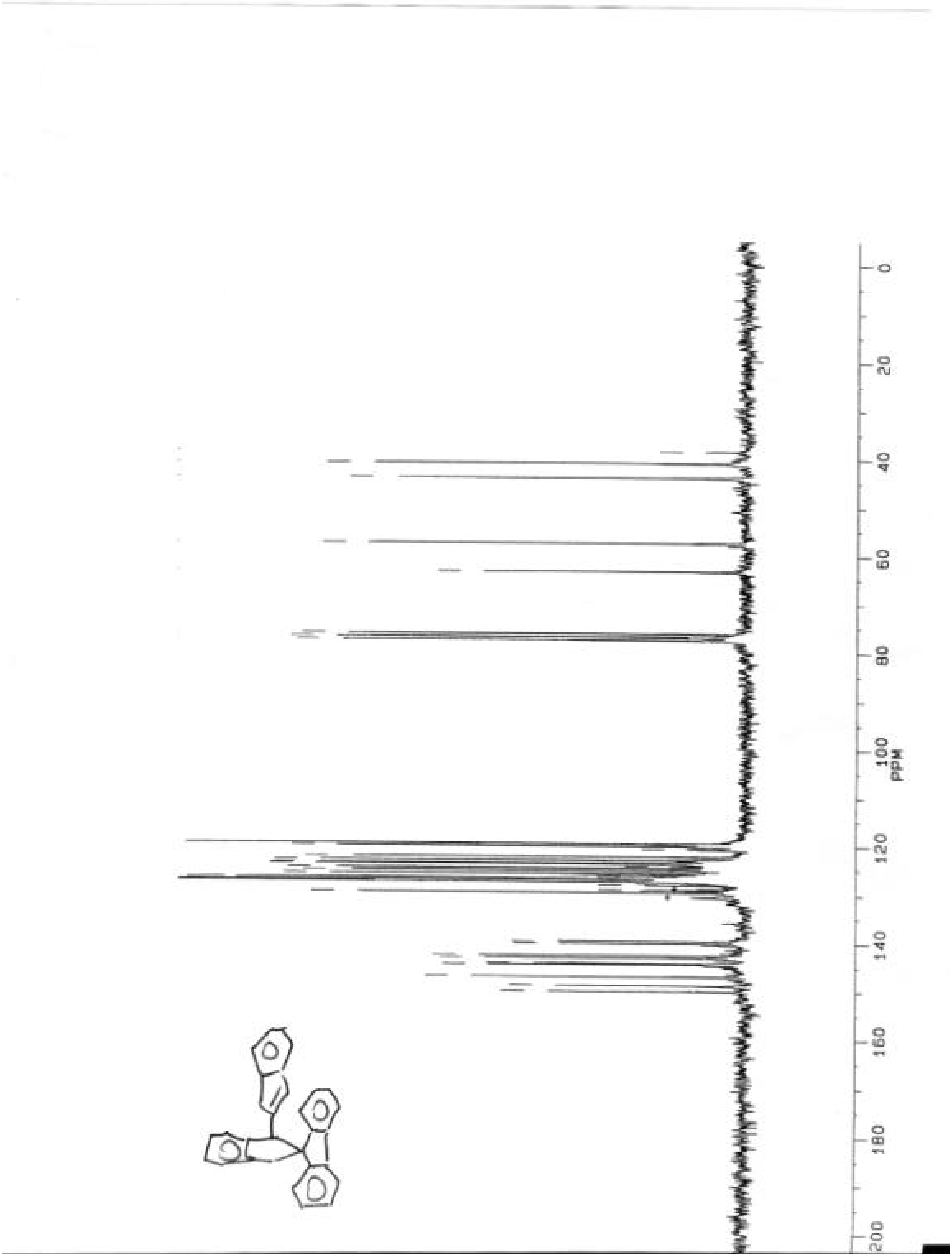
The main product has a m/z = 382, in agreement with the m/z of the desired product **10** ($C_{30}H_{22}$). However, the fragmentation pattern is different from that of **10** obtained earlier via the diGrignard-route (*Scheme 1*). The base peak in the MS spectrum of **10** has an m/z of 278, which represents fragmentation of a neutral C_8H_8 group from the molecular ion. The base peak of the isomer of **10** has a m/z of 217, which represents the fragmentation of a group with a m/z of 165 from the molecular ion. Probably, this fragmentation represents a fluorenyl group. A signal at (m/z = 267 (38% abundance)) clearly indicates fragmentation of an indenyl moiety from the molecular ion. This fragmentation is also present in the mass spectrum of **10** itself (31% abundance) ^{1}H-, ^{13}C- and ^{1}H-^{1}H-COSY and ^{13}C-^{1}H correlation spectroscopy are shown in *figure S1*).

a).

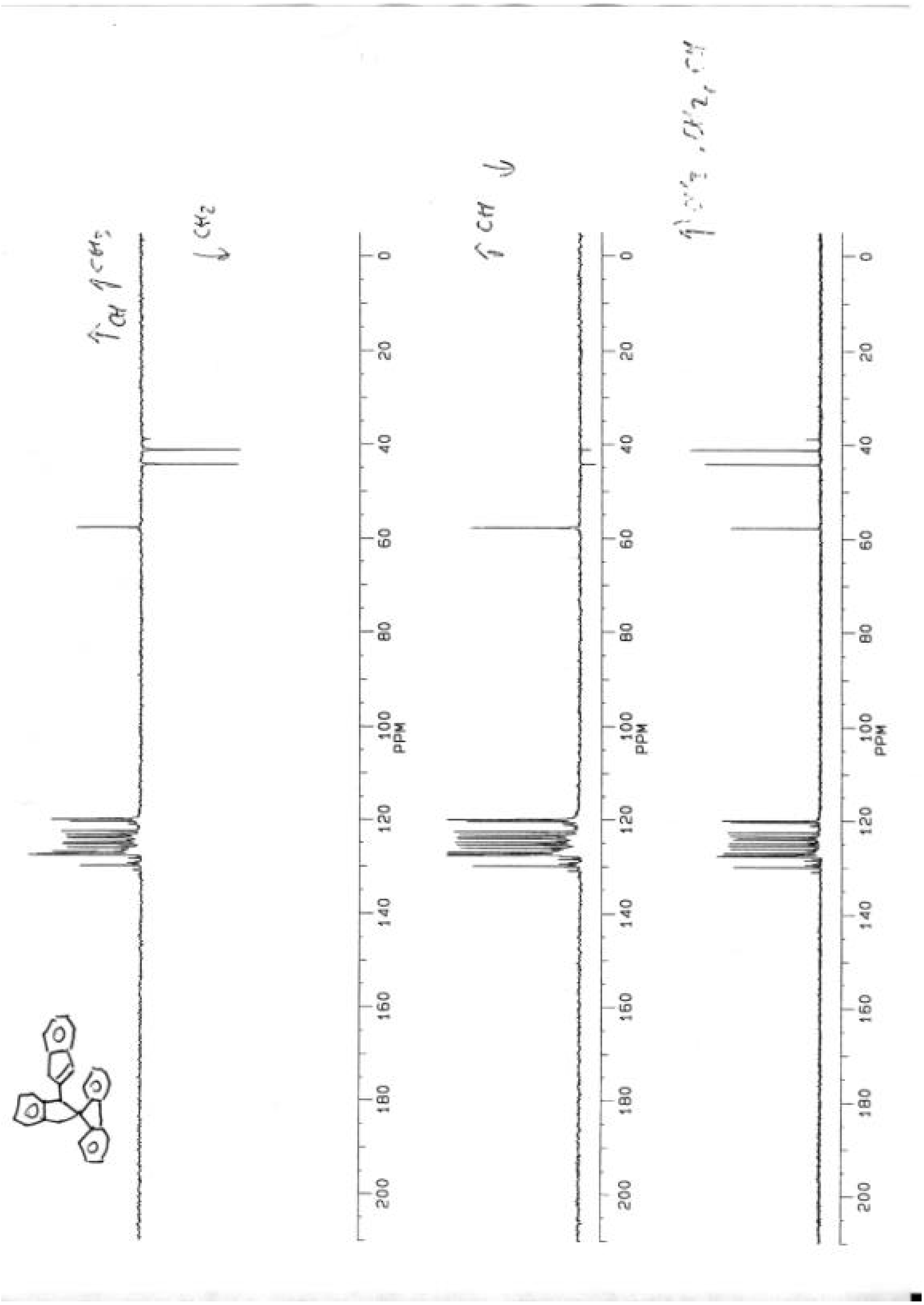


PPM
INTEGRAL
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
43.92
8.17
.53
196.18
impurity
impurity
impurity

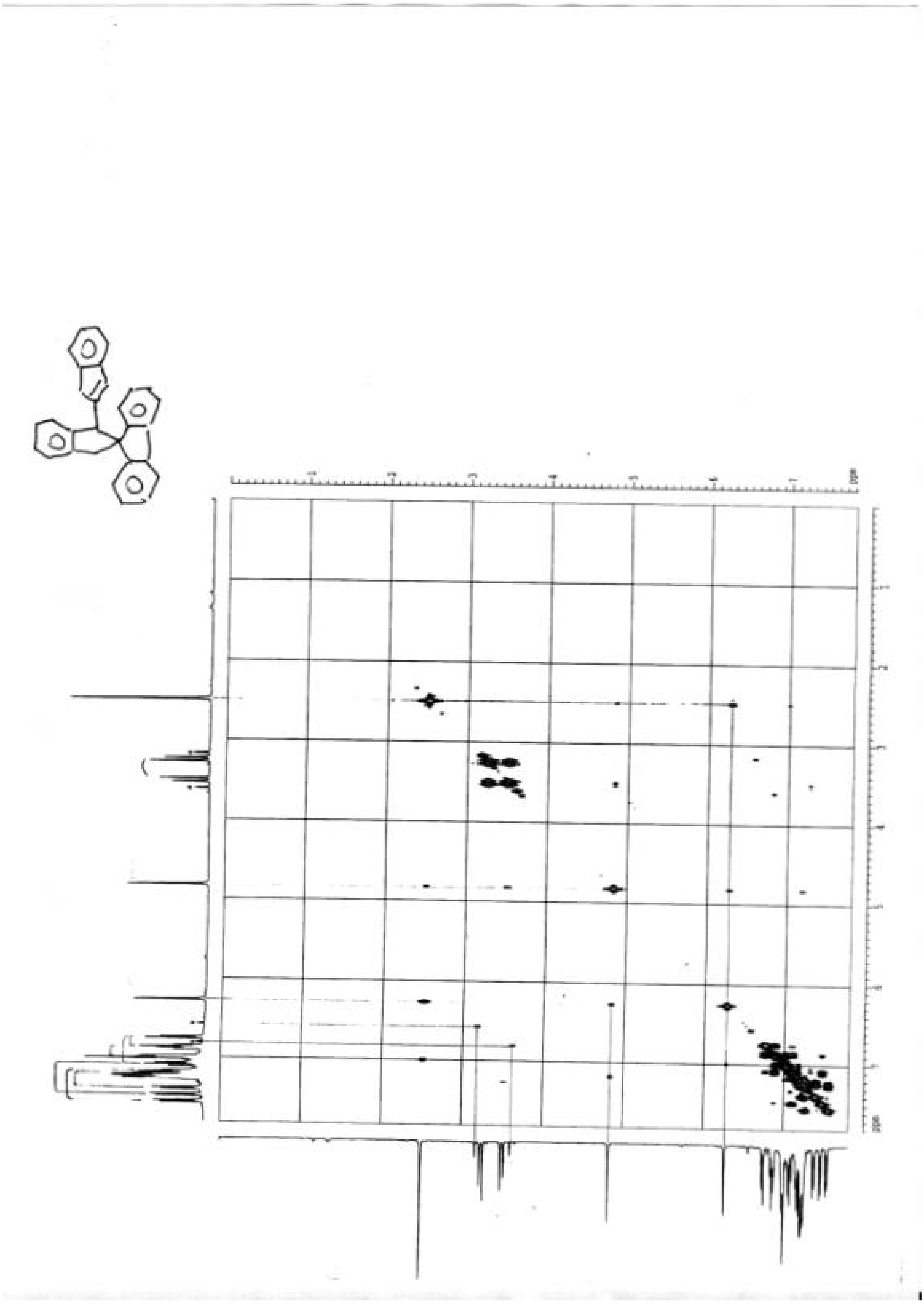
b).



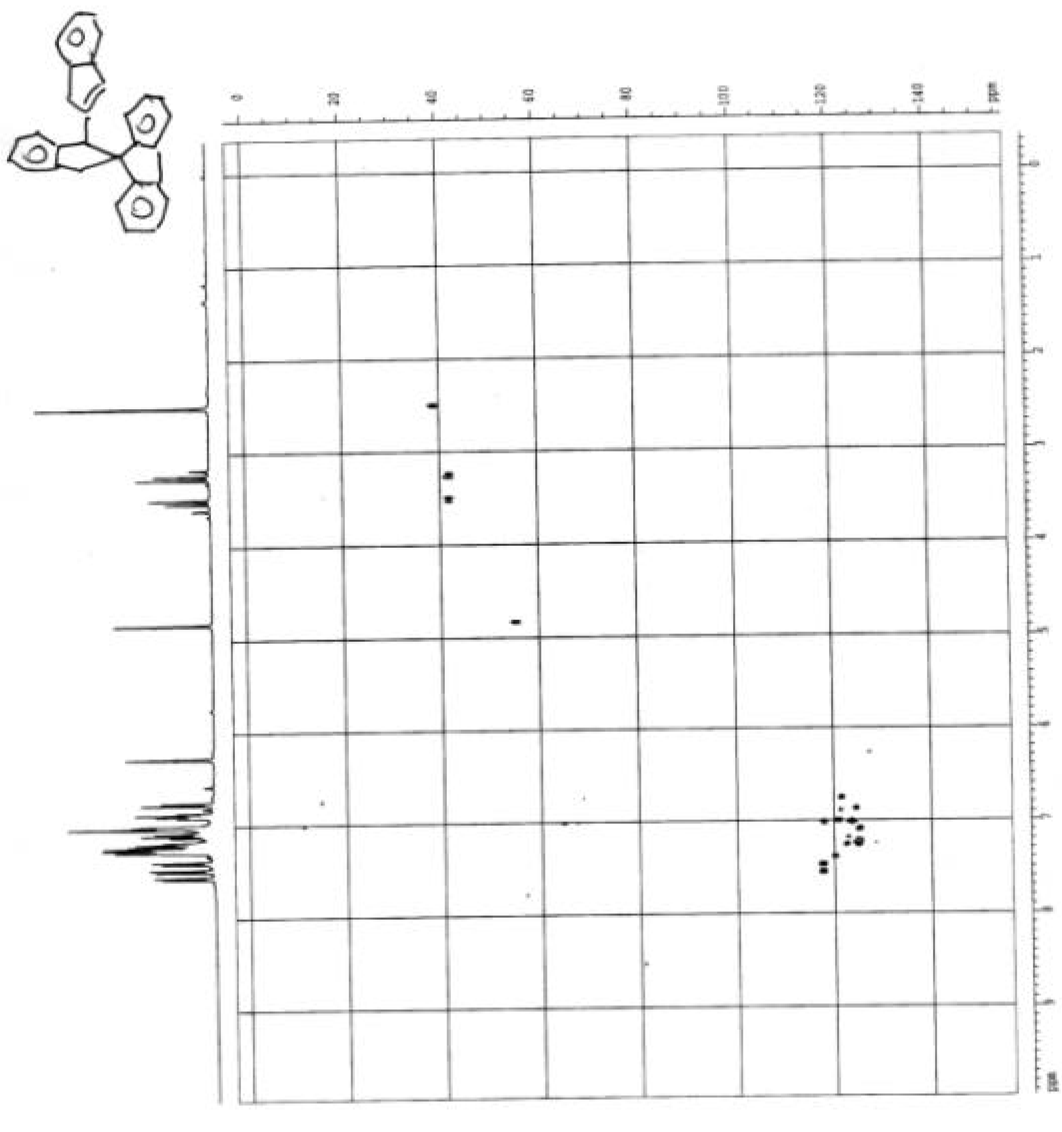
c).



d).



e).



f).

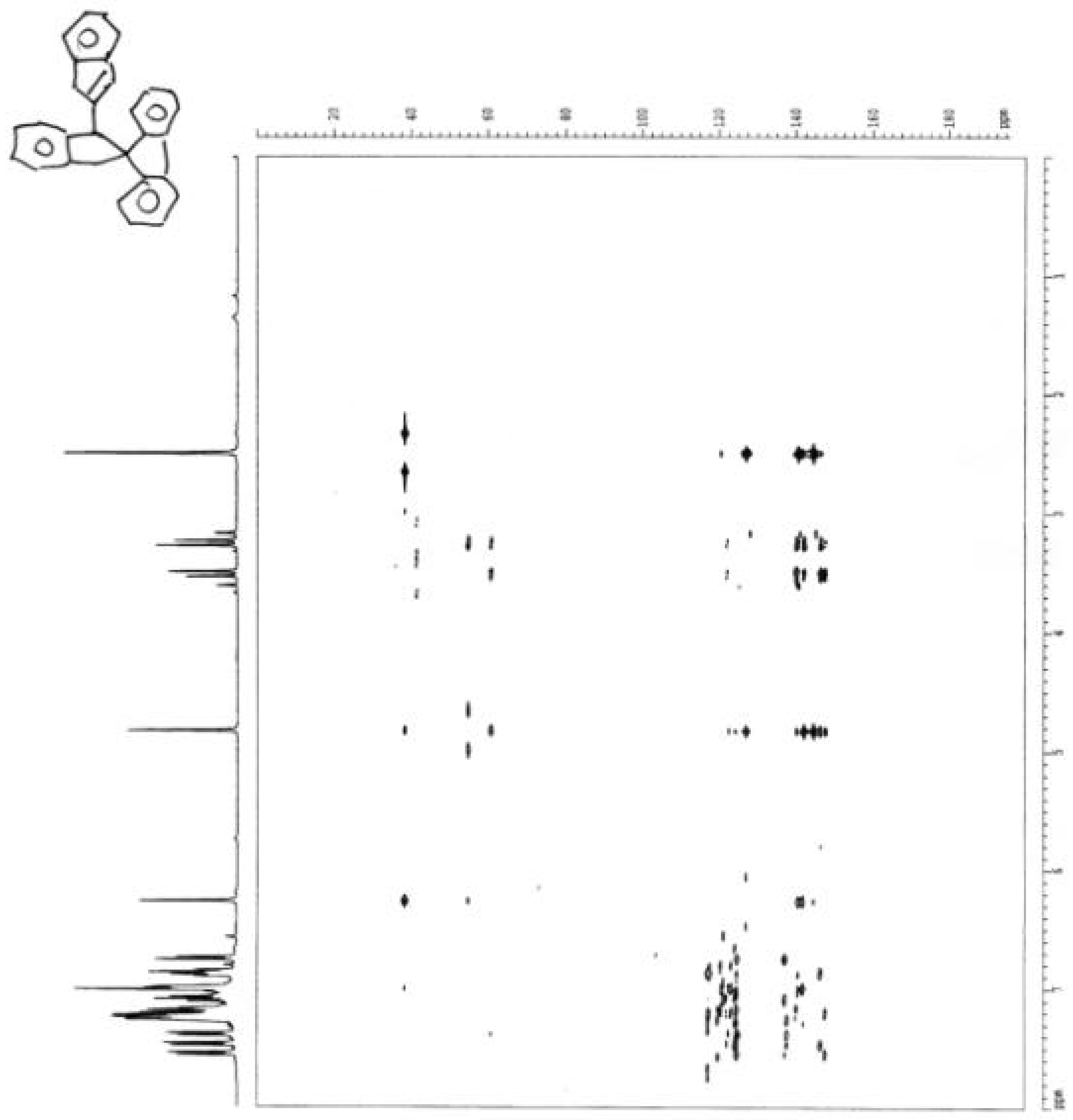


*Figure S1. NMR spectra of **27**. a) ^{1}H-spectrum, b) ^{13}C-spectrum, c) DEPT spectra, d) gradient enhanced ^{1}H-^{1}H-COSY spectrum, e) gradient enhanced ^{1}H-^{13}C correlation spectrum, f) gradient enhanced ^{1}H-^{13}C long-range correlation spectrum.*

The ^{1}H spectrum shows 2 doublets in an AB-pattern at 3.25 (1H) and 3.51 (1H) ppm (J = 15.7 Hz). The large coupling constant of 15.7 Hz suggests a geminal coupling and therefore it indicates the presence of a methylene group containing 2 inequivalent protons. A singlet at 2.50 ppm (2H) can be assigned to a CH_2-group with equivalent protons. The singlet at 4.83 ppm (1H) can be either a deshielded sp^3-proton or a shielded vinylic proton. The singlet at 6.27 ppm (1H) was assigned to a vinylic proton. The ^{13}C-spectrum shows 30 distinguishable peaks (the unknown molecule contains 30 carbon atoms according to the MS spectrum). This indicates that the molecule has almost no symmetry. Important information was also obtained from the DEPT spectra. Positive signals at 41 and 44 ppm in the 45° spectrum confirm the presence of 2 CH_2-groups. Furthermore, 1 positive signal in the 90° is visible at 57 ppm, which represents a CH-signal. There are no CH_3-signals present. Ten signals were assigned to quaternary carbon atoms. Nine of these signals have chemical shifts between 139 and 150 ppm and therefore must come from sp^2 carbons. The signal at 63 ppm must come from a quaternary sp^3-carbon. More information can be derived from the direct ^{13}C-^{1}H correlation spectrum. There is a correlation of the CH_2-signal at 41 ppm in the carbon spectrum with the singlet at 2.50 ppm in the ^{1}H spectrum. Furthermore, there is a correlation between the CH_2-signal at 44 ppm with the AB pattern doublets at 3.25 and 3.51 ppm respectively. This confirms the expectation we got from the ^{1}H spectrum: there is a methylene group with 2 inequivalent protons present in the molecule. So the molecule must contain at least one chiral center. The CH signal at 57 ppm correlates with the singlet at 4.83 ppm. This implies that the latter signal belongs to a deshielded sp^3-proton. There is a correlation of the doublet at 3.51 belonging to one of the inequivalent CH_2-protons with the singlet at 4.83 ppm belonging to the sp^3 CH in the ^1H-^1H correlation spectrum. Remarkably, there is no correlation of the other doublet with the singlet at 4.83 ppm visible in this spectrum. That means that de coupling of one of the inequivalent protons is larger than the coupling constant of the other with the sp^3 CH proton. Besides a small correlation from the doublet at 3.51 ppm with a multiplet at 7.23 ppm, both doublets have a strong internal interaction. This implies that the inequivalent CH_2-group is isolated between two groups of one quaternary carbon atom at least. Since there is a correlation of one of the inequivalent CH_2-protons with the CH sp^3-proton over at least one quaternary carbon atom, a ^4J is present, suggesting a W-coupling. Since there are strong correlations of the quaternary carbon atom with both the sp^3 CH protons and one of the inequivalent CH_2-protons (at 3.25 ppm) it can be concluded that the sole quaternary sp^3 carbon atom is in between these groups. Combining this information it is clear that these atoms must be present in a 5-membered ring containing 2 sp^2 and 3 sp^3 carbon atoms, wherein the sp^3 CH-carbon atom is chiral. The latter carbon atom has a long range correlation with the singlet at 6.27 ppm. This correlation is confirmed by the interaction of the singlet at 6.27 ppm with the singlet belonging to the sp^3 CH at 4.83 ppm. Besides this correlation, there is a small correlation of this signal with a part of the multiplet (3H) at 7.00 ppm and a strong correlation with the singlet at 2.50 ppm (2H), belonging to an indene-moiety. Thus, the chiral sp^3 CH is substituted with an indene moiety. Now, all proton- and carbon signals except the aromatic are assigned. The molecular formula is $C_{30}H_{22}$. Till so far 14 carbon and 10 hydrogen atoms were used. In the reaction were used two 2-indenyl moieties and a biphenyl moiety. Therefore, we propose that the main reaction product is spiro compound **27**. A low quality X-ray structure (R=12.9%) of the corresponding zirconium dichloride complex is shown in *figure S2*, also indicating structure **27** for the compound that was formed (attempts to make single crystals of **27** were unsuccesfull).

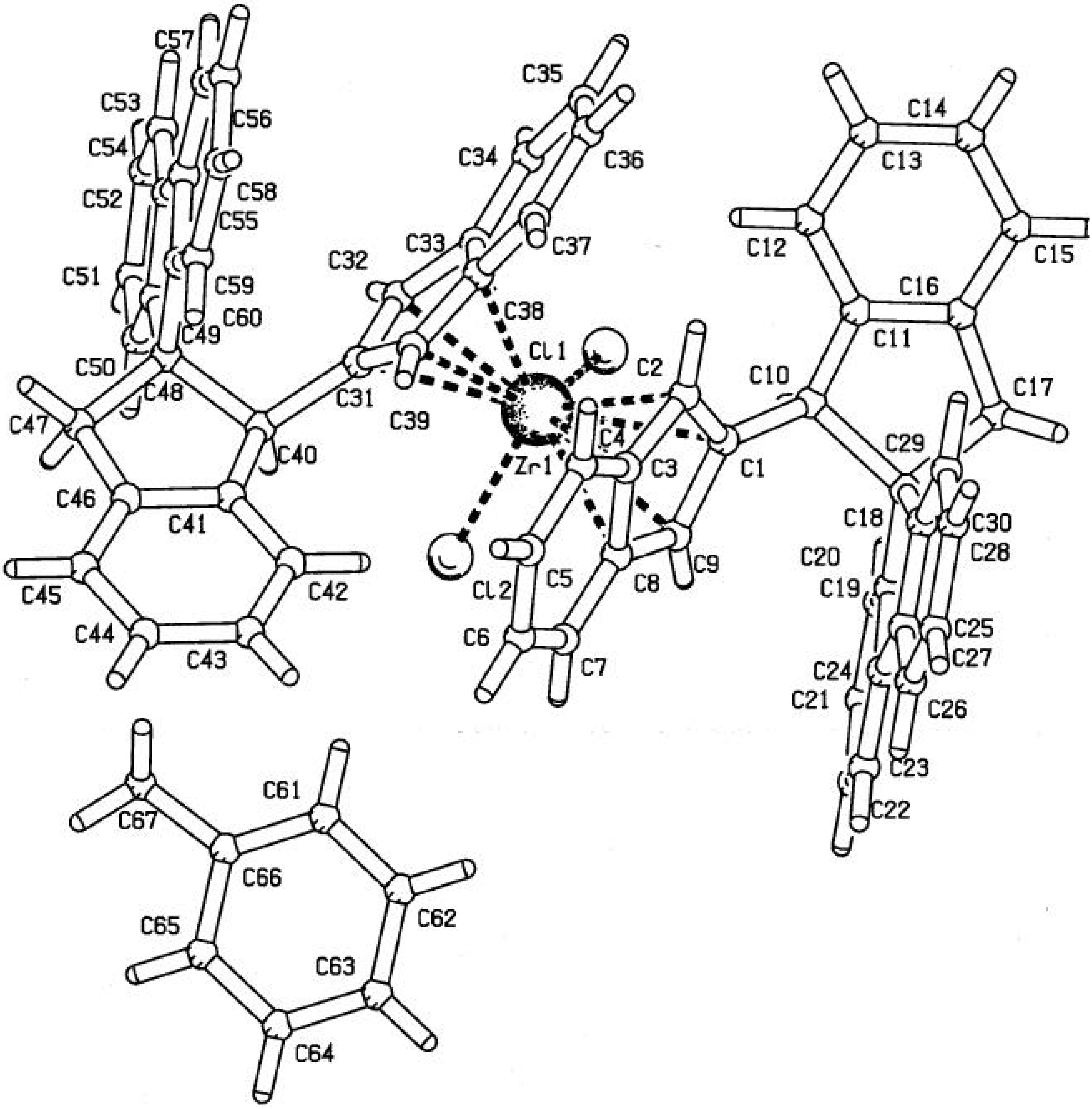


*Figure S2. X-Ray Structure (R=12.9%) of (**27**)$_2$ZrCl$_2$.*

===
S U P P L E M E N T A R Y   M A T E R I A L
===

B E L O N G I N G   TO   T H E   P A P E R

b y

A.L.Spek, Bijvoet Centre for Biomolecular Research,
Utrecht University, Utrecht, The Netherlands.

C o n t e n t s
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REPORT ON THE STRUCTURE DETERMINATION OF C60 H42 Cl2 Zr

The crystal structure was determined for a yellow crystal taken from a toluene solution, covered by inert oil and transferred into the cold N2-stream on an Enraf-Nonius CAD4T (Rotating Anode) diffractometer.

Reflection profiles were highly structured, indicating poor crystal quality. Both attemps to find a higher quality crystal or to provide higher quality crystals were unsuccessful.

In addition, it was not possible to collect a complete dataset. Data collection terminated abruptly due to the desintegration of the crystal. Thus, resolution of the structure in the b-axis direction is in particular rather limited (effecting in particular the precision of bonds in that direction).

In view of the limited number of reflections, it was not possible to refine all positional parameters separately. Parameters for idealized phenyl moieties were refined instead.

The Structure was solved by Patterson Techniques (DIRDIF) followed by structure expansion from numerous difference electron density maps.

The resulting structure should, due to the limited data, only be used qualitatively (i.e. 3D structure and 2D topology). No quantitive conclusions in terms of bond distances and angles should be drawn from this structure. (E.g. The fact that the Zr-Cl distance in this structure in longer by 0.05 Angstrom as compared to similar published structures might well be an artifact.

Anisotropic Displacement Parameters were refined for Zr & Cl, all other non-hydrogen atoms were assigned individual isotropic parameters. Those parameters refined in a number of cases to meaningless values.

Hudrogen atoms were introduced at calculated positions and refined riding on their carrier atoms.

Packing analysis learns that the reported structure is complete (i.e. no voids in the structure) with no unreasonable short intermolecular contacts (usually an indication of unresolved problems).

Table S1 - Crystal Data and Details of the Structure Determination for: s2052a

Crystal Data			
Formula			C60 H42 Cl2 Zr, C7 H8
Formula Weight			1017.19
Crystal System			Monoclinic
Space group		P21/c	(No. 14)
a, b, c [Angstrom]	23.1232(10)	9.0057(10)	24.4778(10)
alpha, beta, gamma [deg]	90	106.909(10)	90
V [Ang**3]			4876.9(7)
Z			4
D(calc) [g/cm**3]			1.385
Mu(MoKa) [/mm]			0.380
F(000)			2104
Data Collection			
Temperature (K)			150
Radiation [Angstrom]		MoKa	0.71073
Theta Min-Max [Deg]			0.9, 20.0
Dataset	0: 22 ;	0: 3 ;	-23: 22
Tot., Uniq. Data, R(int)	2406,	2352,	0.094
Observed data [I > 2.0 sigma(I)]			1293
Refinement			
Nref, Npar			2352, 230
R, wR, S			0.1286, 0.3617, 1.15
w = 1/[\s^2^(Fo^2^)+(0.2000P)^2^]			where P=(Fo^2^+2Fc^2^)/3
Max. and Av. Shift/Error			2.93, 0.09
Min. and Max. resd. dens. [e/Ang^3]			-0.54, 1.33

Table S2 - Final Coordinates and Equivalent Isotropic Displacement Parameters of the non-Hydrogen atoms for: s2052a

Atom	x	y	z	U(eq) [Ang^2]
Zr1	0.23923(11)	0.3038(7)	0.50158(10)	0.058(3)
Cl1	0.2154(3)	0.4336(17)	0.5826(3)	0.041(7)
Cl2	0.2151(3)	0.5318(17)	0.4414(3)	0.030(7)
C1	0.3433(9)	0.313(4)	0.5738(10)	0.050(7)
C2	0.3346(10)	0.171(5)	0.5492(9)	0.011(8)
C3	0.3361(7)	0.190(4)	0.4942(6)	0.009(8)
C4	0.3381(7)	0.080(3)	0.4547(9)	0.031(11)
C5	0.3432(7)	0.120(3)	0.4015(7)	0.023(9)
C6	0.3464(6)	0.269(3)	0.3877(6)	0.002(7)
C7	0.3443(7)	0.378(3)	0.4272(9)	0.053(13)
C8	0.3392(7)	0.339(3)	0.4805(7)	0.011(8)
C9	0.3425(12)	0.413(5)	0.5297(10)	0.048(14)
C10	0.3591(13)	0.354(6)	0.6375(11)	0.030(9)
C11	0.3596(7)	0.256(3)	0.6799(6)	0.009(7)
C12	0.3194(6)	0.139(3)	0.6757(6)	0.032(9)
C13	0.3289(8)	0.035(2)	0.7196(8)	0.032(9)
C14	0.3786(8)	0.049(3)	0.7676(7)	0.023(8)
C15	0.4188(6)	0.166(3)	0.7718(6)	0.023(8)
C16	0.4093(7)	0.270(3)	0.7280(7)	0.013(7)
C17	0.4435(13)	0.408(6)	0.7258(11)	0.028(9)
C18	0.4276(11)	0.440(6)	0.6580(11)	0.021(8)
C19	0.4312(8)	0.596(3)	0.6380(7)	0.026(9)
C20	0.4041(7)	0.723(3)	0.6510(7)	0.017(8)
C21	0.4111(8)	0.858(3)	0.6258(9)	0.033(10)
C22	0.4452(8)	0.865(3)	0.5875(8)	0.030(9)
C23	0.4723(7)	0.737(3)	0.5744(7)	0.026(9)

Table S2 - Final Coordinates and Equivalent Isotropic Displacement Parameters of the non-Hydrogen atoms (continued) for: s2052a

Atom	x	y	z	U(eq) [Ang^2]
C24	0.4653(7)	0.603(3)	0.5997(8)	0.014(8)
C25	0.4906(8)	0.446(3)	0.5986(8)	0.023(8)
C26	0.5300(8)	0.398(3)	0.5690(6)	0.034(10)
C27	0.5505(7)	0.252(3)	0.5748(7)	0.015(8)
C28	0.5315(8)	0.154(3)	0.6103(8)	0.042(11)
C29	0.4921(8)	0.203(3)	0.6399(7)	0.031(9)
C30	0.4717(7)	0.349(3)	0.6340(7)	0.013(8)
C31	0.1496(10)	0.212(4)	0.4247(9)	0.007(7)
C32	0.1329(10)	0.235(4)	0.4755(8)	0.017(8)
C33	0.1664(9)	0.141(3)	0.5157(9)	0.039(10)
C34	0.1617(9)	0.095(3)	0.5684(9)	0.046(11)
C35	0.1914(10)	-0.033(3)	0.5938(7)	0.056(12)
C36	0.2259(10)	-0.114(3)	0.5664(10)	0.059(12)
C37	0.2306(9)	-0.068(3)	0.5137(10)	0.076(14)
C38	0.2008(10)	0.060(3)	0.4884(7)	0.042(10)
C39	0.1945(12)	0.099(4)	0.4340(9)	0.030(9)
C40	0.1136(10)	0.296(7)	0.3679(11)	0.019(10)
C41	0.1382(6)	0.269(4)	0.3187(5)	0.016(8)
C42	0.1981(5)	0.275(3)	0.3183(5)	0.010(7)
C43	0.2123(5)	0.264(3)	0.2670(6)	0.020(9)
C44	0.1665(6)	0.246(3)	0.2162(5)	0.034(10)
C45	0.1066(6)	0.239(3)	0.2165(5)	0.025(9)
C46	0.0924(5)	0.251(4)	0.2678(6)	0.026(9)
C47	0.0330(14)	0.256(5)	0.2799(11)	0.025(9)
C48	0.0482(12)	0.231(6)	0.3443(11)	0.023(9)
C49	0.0050(7)	0.276(3)	0.3734(7)	0.015(8)

Table S2 - Final Coordinates and Equivalent Isotropic Displacement Parameters of the non-Hydrogen atoms (continued) for: s2052a

Atom	x	y	z	U(eq) [Ang^2]
C50	-0.0163(8)	0.420(3)	0.3747(7)	0.025(9)
C51	-0.0561(9)	0.452(3)	0.4061(8)	0.038(11)
C52	-0.0747(7)	0.340(3)	0.4362(7)	0.020(8)
C53	-0.0534(8)	0.196(3)	0.4349(7)	0.031(9)
C54	-0.0136(8)	0.164(3)	0.4035(8)	0.024(9)
C55	0.0145(8)	0.038(4)	0.3950(9)	0.039(10)
C56	0.0122(9)	-0.099(4)	0.4199(8)	0.038(10)
C57	0.0450(11)	-0.218(4)	0.4080(10)	0.064(13)
C58	0.0802(10)	-0.199(4)	0.3711(11)	0.069(14)
C59	0.0825(8)	-0.061(5)	0.3462(8)	0.049(11)
C60	0.0496(10)	0.057(4)	0.3581(9)	0.036(10)
C61	0.2402(7)	0.697(3)	0.3016(7)	0.053(11)
C62	0.2980(6)	0.757(3)	0.3156(7)	0.030(9)
C63	0.3133(7)	0.857(3)	0.2787(9)	0.049(11)
C64	0.2707(9)	0.897(3)	0.2279(9)	0.078(14)
C65	0.2128(7)	0.837(3)	0.2140(7)	0.035(10)
C66	0.1976(5)	0.737(3)	0.2509(6)	0.011(7)
C67	0.1356(6)	0.692(4)	0.2327(10)	0.064(15)

U(eq) = 1/3 of the trace of the orthogonalized U Tensor

Table S3 - Hydrogen Atom Positions and Isotropic Displacement Parameters for: s2052a

Atom	x	y	z	U(iso) [Ang^2]
H2	0.32900	0.08280	0.56660	0.05(11)
H4	0.33600	-0.01920	0.46390	0.05(8)
H5	0.34460	0.04710	3/8	0.07(11)
H6	0.34980	0.29570	0.35210	0.05(6)
H7	0.34640	0.47810	0.41800	0.05(7)
H9	0.34410	0.51620	0.53360	0.05(8)
H10	0.32970	0.43060	0.63990	0.2(2)
H12	0.28620	0.12990	0.64360	0.2(2)
H13	0.30200	-0.04290	0.71670	0.06(10)
H14	0.38490	-0.02030	0.79690	0.3(3)
H15	0.45200	0.17520	0.80400	0.08(12)
H17A	0.48650	0.39300	0.74270	0.5(5)
H17B	0.43010	0.48850	0.74540	0.9(12)
H20	0.38130	0.71890	0.67660	0.06(10)
H21	0.39300	0.94330	0.63450	0.2(2)
H22	0.44990	0.95460	0.57060	0.3(3)
H23	0.49510	0.74160	0.54880	0.05(6)
H26	0.54270	0.46250	0.54530	0.03(8)
H27	0.57680	0.21890	0.55500	0.05(6)
H28	0.54520	0.05680	0.61420	0.03(9)
H29	0.47940	0.13830	0.66360	0.05(6)
H32	0.10410	0.30140	0.48030	0.0200
H34	0.13860	0.14960	0.58680	0.0550
H35	0.18820	-0.06360	0.62900	0.0680
H36	0.24570	-0.19950	0.58330	0.0710
H37	0.25360	-0.12220	0.49540	0.0920

Table S3 - Hydrogen Atom Positions and Isotropic Displacement Parameters (continued) for: s2052a

Atom	x	y	z	U(iso) [Ang^2]
H39	0.21420	0.06160	0.40890	0.0360
H40	0.11190	0.40280	3/8	0.05(11)
H42	0.22880	0.28760	0.35240	0.05(6)
H43	0.25240	0.26800	0.26680	0.05(6)
H44	0.17600	0.23770	0.18190	0.04(9)
H45	0.07590	0.22700	0.18250	0.03(8)
H47A	0.00640	0.17860	0.25910	0.04(9)
H47B	0.01360	0.35150	0.26930	0.05(7)
H50	-0.00380	0.49500	0.35460	0.10(14)
H51	-0.07030	0.54810	0.40700	0.05(7)
H52	-0.10130	0.36090	0.45720	0.04(9)
H53	-0.06590	0.12060	0.45500	0.06(11)
H56	-0.01140	-0.11210	0.44460	2(3)
H57	0.04340	-0.31010	0.42470	0.05(11)
H58	0.10210	-0.27840	0.36320	0.05(6)
H59	0.10600	-0.04860	0.32150	2(3)
H61	0.22990	0.63040	0.32630	0.05(6)
H62	0.32650	0.73040	0.34950	0.10(13)
H63	0.35200	0.89700	0.28800	0.8(10)
H64	0.28090	0.96370	0.20330	2(3)
H65	0.18430	0.86370	0.18000	2(4)
H67A	0.11360	0.74400	0.25470	0.05(6)
H67B	0.13300	0.58720	0.23830	0.05(7)
H67C	0.11850	0.71520	0.19300	2(4)

The Temperature Factor has the Form of Exp(-T) Where
T = 8*(Pi**2)*U*(Sin(Theta)/Lambda)**2 for Isotropic Atoms

Table S4 - (An)isotropic Displacement Parameters for: s2052a

Atom	U(1,1) or U	U(2,2)	U(3,3)	U(2,3)	U(1,3)	U(1,2)
Zr1	0.0000(14)	0.170(10)	0.0038(15)	0.007(3)	-0.0020(10)	0.000(3)
Cl1	0.013(4)	0.09(2)	0.019(4)	-0.011(7)	0.001(3)	-0.009(6)
Cl2	0.032(5)	0.02(2)	0.036(5)	0.012(7)	0.006(3)	0.002(7)

The Temperature Factor has the Form of Exp(-T) Where
T = 8*(Pi**2)*U*(Sin(Theta)/Lambda)**2 for Isotropic Atoms
T = 2*(Pi**2)*Sumij(h(i)*h(j)*U(i,j)*Astar(i)*Astar(j)), for Anisotropic Atoms. Astar(i) are Reciprocal Axial Lengths and h(i) are the Reflection Indices.

Table S5 - Bond Distances (Angstrom)
for: s2052a

Zr1	-Cl1	2.498(10)	C13	-C14	1.39(3)
Zr1	-Cl2	2.494(14)	C14	-C15	1.39(3)
Zr1	-C1	2.54(2)	C15	-C16	1.39(3)
Zr1	-C2	2.48(3)	C16	-C17	1.48(5)
Zr1	-C3	2.52(2)	C17	-C18	1.62(4)
Zr1	-C8	2.531(17)	C18	-C19	1.50(6)
Zr1	-C9	2.49(3)	C18	-C30	1.55(4)
Zr1	-C31	2.50(2)	C19	-C20	1.38(3)
Zr1	-C32	2.43(2)	C19	-C24	1.39(3)
Zr1	-C33	2.33(2)	C20	-C21	1.39(4)
Zr1	-C38	2.36(3)	C21	-C22	1.39(3)
Zr1	-C39	2.49(3)	C22	-C23	1.39(3)
C1	-C2	1.40(5)	C23	-C24	1.39(4)
C1	-C9	1.40(5)	C24	-C25	1.53(4)
C1	-C10	1.54(4)	C25	-C26	1.39(3)
C2	-C3	1.37(3)	C25	-C30	1.39(3)
C3	-C4	1.39(4)	C26	-C27	1.39(4)
C3	-C8	1.39(4)	C27	-C28	1.40(3)
C4	-C5	1.39(3)	C28	-C29	1.39(3)
C5	-C6	1.39(4)	C29	-C30	1.39(4)
C6	-C7	1.39(3)	C31	-C32	1.42(3)
C7	-C8	1.39(3)	C31	-C39	1.42(4)
C8	-C9	1.36(4)	C31	-C40	1.59(5)
C10	-C11	1.36(5)	C32	-C33	1.36(4)
C10	-C18	1.70(5)	C33	-C34	1.39(3)
C11	-C12	1.39(3)	C33	-C38	1.39(3)
C11	-C16	1.39(2)	C34	-C35	1.39(4)
C12	-C13	1.39(3)	C35	-C36	1.39(3)

Table S5 - Bond Distances (Angstrom) (continued)
for: s2052a

C36	-C37	1.39(3)	C2	-H2	0.9280
C37	-C38	1.39(4)	C4	-H4	0.9260
C38	-C39	1.34(3)	C5	-H5	0.9301
C40	-C41	1.49(3)	C6	-H6	0.9291
C40	-C48	1.57(5)	C7	-H7	0.9339
C41	-C42	1.389(19)	C9	-H9	0.9339
C41	-C46	1.390(19)	C10	-H10	0.9822
C42	-C43	1.391(18)	C12	-H12	0.9287
C43	-C44	1.389(19)	C13	-H13	0.9265
C44	-C45	1.39(2)	C14	-H14	0.9297
C45	-C46	1.391(19)	C15	-H15	0.9303
C46	-C47	1.49(4)	C17	-H17A	0.9689
C47	-C48	1.53(4)	C17	-H17B	0.9686
C48	-C49	1.44(4)	C20	-H20	0.9296
C48	-C60	1.60(6)	C21	-H21	0.9287
C49	-C50	1.39(4)	C22	-H22	0.9275
C49	-C54	1.39(3)	C23	-H23	0.9298
C50	-C51	1.39(3)	C26	-H26	0.9270
C51	-C52	1.39(3)	C27	-H27	0.9301
C52	-C53	1.39(4)	C28	-H28	0.9263
C53	-C54	1.39(3)	C29	-H29	0.9281
C54	-C55	1.35(4)	C32	-H32	0.9276
C55	-C56	1.38(5)	C34	-H34	0.9327
C55	-C60	1.39(3)	C35	-H35	0.9278
C56	-C57	1.39(4)	C36	-H36	0.9292
C57	-C58	1.39(4)	C37	-H37	0.9275
C58	-C59	1.39(5)	C39	-H39	0.9280
C59	-C60	1.39(5)	C40	-H40	0.9802

Table S5 - Bond Distances (Angstrom) (continued)
for: s2052a

C42	-H42	0.9321	C61	-C66	1.39(2)
C43	-H43	0.9294	C62	-C63	1.39(3)
C44	-H44	0.9306	C63	-C64	1.39(3)
C45	-H45	0.9298	C64	-C65	1.39(3)
C47	-H47A	0.9702	C65	-C66	1.39(3)
C47	-H47B	0.9698	C66	-C67	1.43(2)
C50	-H50	0.9298	C61	-H61	0.9305
C51	-H51	0.9282	C62	-H62	0.9285
C52	-H52	0.9284	C63	-H63	0.9294
C53	-H53	0.9324	C64	-H64	0.9283
C56	-H56	0.9323	C65	-H65	0.9304
C57	-H57	0.9302	C67	-H67A	0.9630
C58	-H58	0.9285	C67	-H67B	0.9581
C59	-H59	0.9297	C67	-H67C	0.9596
C61	-C62	1.39(3)			

Table S6 - Bond Angles (Degrees)
for: s2052a

Cl1	-Zr1	-Cl2	91.2(4)	C1	-Zr1	-C38	111.7(10)
Cl1	-Zr1	-C1	79.4(6)	C1	-Zr1	-C39	127.8(11)
Cl1	-Zr1	-C2	102.9(6)	C2	-Zr1	-C3	31.7(6)
Cl1	-Zr1	-C3	130.8(4)	C2	-Zr1	-C8	54.3(9)
Cl1	-Zr1	-C8	121.9(6)	C2	-Zr1	-C9	53.8(13)
Cl1	-Zr1	-C9	90.6(7)	C2	-Zr1	-C31	128.5(12)
Cl1	-Zr1	-C31	115.2(6)	C2	-Zr1	-C32	133.8(12)
Cl1	-Zr1	-C32	83.6(6)	C2	-Zr1	-C33	102.0(11)
Cl1	-Zr1	-C33	80.9(6)	C2	-Zr1	-C38	82.1(11)
Cl1	-Zr1	-C38	112.5(6)	C2	-Zr1	-C39	95.5(11)
Cl1	-Zr1	-C39	136.8(7)	C3	-Zr1	-C8	32.0(10)
Cl2	-Zr1	-C1	112.8(8)	C3	-Zr1	-C9	51.5(12)
Cl2	-Zr1	-C2	133.6(8)	C3	-Zr1	-C31	111.8(8)
Cl2	-Zr1	-C3	110.1(7)	C3	-Zr1	-C32	136.9(11)
Cl2	-Zr1	-C8	80.6(6)	C3	-Zr1	-C33	116.8(10)
Cl2	-Zr1	-C9	82.5(9)	C3	-Zr1	-C38	85.3(10)
Cl2	-Zr1	-C31	80.4(8)	C3	-Zr1	-C39	81.8(9)
Cl2	-Zr1	-C32	91.1(8)	C8	-Zr1	-C9	31.4(8)

Cl2	-Zr1	-C33	123.9(6)	C8	-Zr1	-C31	119.6(7)
Cl2	-Zr1	-C38	132.5(5)	C8	-Zr1	-C32	153.1(6)
Cl2	-Zr1	-C39	103.8(7)	C8	-Zr1	-C33	148.3(9)
C1	-Zr1	-C2	32.4(12)	C8	-Zr1	-C38	114.8(9)
C1	-Zr1	-C3	51.7(8)	C8	-Zr1	-C39	100.6(8)
C1	-Zr1	-C8	53.2(6)	C9	-Zr1	-C31	149.1(8)
C1	-Zr1	-C9	32.4(10)	C9	-Zr1	-C32	171.3(13)
C1	-Zr1	-C31	160.9(11)	C9	-Zr1	-C33	152.1(9)
C1	-Zr1	-C32	150.6(8)	C9	-Zr1	-C38	134.4(12)
C1	-Zr1	-C33	119.7(9)	C9	-Zr1	-C39	131.0(10)

Table S6 - Bond Angles (Degrees) (continued)
for: s2052a

C31	-Zr1	-C32	33.4(7)	C6	-C7	-C8	120(2)
C31	-Zr1	-C33	55.1(8)	Zr1	-C8	-C3	73.5(11)
C31	-Zr1	-C38	52.5(9)	Zr1	-C8	-C7	123.7(12)
C31	-Zr1	-C39	33.1(10)	Zr1	-C8	-C9	72.5(15)
C32	-Zr1	-C33	33.0(9)	C3	-C8	-C7	120(2)
C32	-Zr1	-C38	54.2(10)	C3	-C8	-C9	105(2)
C32	-Zr1	-C39	56.3(10)	C7	-C8	-C9	135(3)
C33	-Zr1	-C38	34.4(8)	Zr1	-C9	-C1	75.9(17)
C33	-Zr1	-C39	57.0(8)	Zr1	-C9	-C8	76.1(16)
C38	-Zr1	-C39	32.0(8)	C1	-C9	-C8	111(3)
Zr1	-C1	-C2	71.5(14)	C1	-C10	-C11	124(4)
Zr1	-C1	-C9	71.8(15)	C1	-C10	-C18	110(2)
Zr1	-C1	-C10	127.6(17)	C11	-C10	-C18	106(2)
C2	-C1	-C9	107(2)	C10	-C11	-C12	125(2)
C2	-C1	-C10	128(3)	C10	-C11	-C16	114(2)
C9	-C1	-C10	125(3)	C12	-C11	-C16	120.1(19)
Zr1	-C2	-C1	76.1(18)	C11	-C12	-C13	120.0(14)
Zr1	-C2	-C3	75.6(15)	C12	-C13	-C14	119.8(18)

C1	-C2	-C3	105(3)	C13	-C14	-C15	120.2(19)
Zr1	-C3	-C2	72.7(15)	C14	-C15	-C16	120.1(15)
Zr1	-C3	-C4	123.3(12)	C11	-C16	-C15	120(2)
Zr1	-C3	-C8	74.6(13)	C11	-C16	-C17	111(2)
C2	-C3	-C4	128(3)	C15	-C16	-C17	128.7(18)
C2	-C3	-C8	112(3)	C16	-C17	-C18	103(3)
C4	-C3	-C8	120.3(17)	C10	-C18	-C17	98(2)
C3	-C4	-C5	120(2)	C10	-C18	-C19	118(3)
C4	-C5	-C6	120(2)	C10	-C18	-C30	108(3)
C5	-C6	-C7	119.9(16)	C17	-C18	-C19	119(3)

Table S6 - Bond Angles (Degrees) (continued) for: s2052a

C17	-C18	-C30	108(3)	Zr1	-C32	-C31	75.9(14)
C19	-C18	-C30	105(2)	Zr1	-C32	-C33	69.4(14)
C18	-C19	-C20	128.9(19)	C31	-C32	-C33	107(2)
C18	-C19	-C24	111(2)	Zr1	-C33	-C32	77.6(16)
C20	-C19	-C24	120(2)	Zr1	-C33	-C34	125.4(16)
C19	-C20	-C21	120.0(17)	Zr1	-C33	-C38	73.7(14)
C20	-C21	-C22	120(2)	C32	-C33	-C34	133(2)
C21	-C22	-C23	120(2)	C32	-C33	-C38	105.4(19)
C22	-C23	-C24	119.9(17)	C34	-C33	-C38	120(2)
C19	-C24	-C23	120(2)	C33	-C34	-C35	120(2)
C19	-C24	-C25	105(2)	C34	-C35	-C36	119.8(19)
C23	-C24	-C25	134.4(17)	C35	-C36	-C37	120(2)
C24	-C25	-C26	127(2)	C36	-C37	-C38	120(2)
C24	-C25	-C30	112.2(18)	Zr1	-C38	-C33	71.9(15)
C26	-C25	-C30	120(2)	Zr1	-C38	-C37	126.3(16)
C25	-C26	-C27	120(2)	Zr1	-C38	-C39	79.6(19)
C26	-C27	-C28	120.1(18)	C33	-C38	-C37	120.0(19)
C27	-C28	-C29	120(2)	C33	-C38	-C39	115(2)

C28	-C29	-C30	120(2)	C37	-C38	-C39	124(2)
C18	-C30	-C25	105(3)	Zr1	-C39	-C31	73.7(17)
C18	-C30	-C29	135(2)	Zr1	-C39	-C38	68.4(16)
C25	-C30	-C29	120.1(18)	C31	-C39	-C38	102(2)
Zr1	-C31	-C32	70.7(13)	C31	-C40	-C41	114(3)
Zr1	-C31	-C39	73.1(15)	C31	-C40	-C48	110(3)
Zr1	-C31	-C40	128(3)	C41	-C40	-C48	101(2)
C32	-C31	-C39	110(2)	C40	-C41	-C42	127.9(15)
C32	-C31	-C40	119(3)	C40	-C41	-C46	111.8(15)
C39	-C31	-C40	131(2)	C42	-C41	-C46	120.0(12)

Table S6 - Bond Angles (Degrees) (continued)
for: s2052a

C41	-C42	-C43	120.1(11)	C56	-C57	-C58	120(3)
C42	-C43	-C44	119.9(12)	C57	-C58	-C59	120(3)
C43	-C44	-C45	120.2(11)	C58	-C59	-C60	120(2)
C44	-C45	-C46	119.9(12)	C48	-C60	-C55	106(3)
C41	-C46	-C45	120.0(12)	C48	-C60	-C59	133(2)
C41	-C46	-C47	109.0(15)	C55	-C60	-C59	120(3)
C45	-C46	-C47	131.0(15)	Zr1	-C2	-H2	113.86
C46	-C47	-C48	105(2)	C1	-C2	-H2	127.23
C40	-C48	-C47	103(3)	C3	-C2	-H2	127.29
C40	-C48	-C49	116(3)	C3	-C4	-H4	120.14
C40	-C48	-C60	109(3)	C5	-C4	-H4	120.20
C47	-C48	-C49	119(3)	C4	-C5	-H5	120.04
C47	-C48	-C60	110(3)	C6	-C5	-H5	119.77
C49	-C48	-C60	98(3)	C5	-C6	-H6	120.16
C48	-C49	-C50	125(3)	C7	-C6	-H6	119.98
C48	-C49	-C54	115(3)	C6	-C7	-H7	119.98
C50	-C49	-C54	119.9(17)	C8	-C7	-H7	119.68
C49	-C50	-C51	120(2)	Zr1	-C9	-H9	115.34

C50	-C51	-C52	120(2)	C1	-C9	-H9	124.71
C51	-C52	-C53	119.9(18)	C8	-C9	-H9	124.68
C52	-C53	-C54	120(2)	C1	-C10	-H10	105.34
C49	-C54	-C53	120(2)	C11	-C10	-H10	105.22
C49	-C54	-C55	106.9(19)	C18	-C10	-H10	105.29
C53	-C54	-C55	133(2)	C11	-C12	-H12	120.02
C54	-C55	-C56	127(2)	C13	-C12	-H12	119.94
C54	-C55	-C60	113(3)	C12	-C13	-H13	119.87
C56	-C55	-C60	120(3)	C14	-C13	-H13	120.34
C55	-C56	-C57	120(2)	C13	-C14	-H14	119.79

Table S6 - Bond Angles (Degrees) (continued)
for: s2052a

C15	-C14	-H14	120.05	C35	-C34	-H34	119.88
C14	-C15	-H15	119.99	C34	-C35	-H35	119.89
C16	-C15	-H15	119.94	C36	-C35	-H35	120.30
C16	-C17	-H17A	111.08	C35	-C36	-H36	119.87
C16	-C17	-H17B	111.01	C37	-C36	-H36	119.94
C18	-C17	-H17A	111.20	C36	-C37	-H37	120.15
C18	-C17	-H17B	111.39	C38	-C37	-H37	120.00
H17A	-C17	-H17B	109.22	Zr1	-C39	-H39	121.27
C19	-C20	-H20	120.35	C31	-C39	-H39	128.97
C21	-C20	-H20	119.64	C38	-C39	-H39	128.96
C20	-C21	-H21	120.13	C31	-C40	-H40	110.48
C22	-C21	-H21	119.91	C41	-C40	-H40	110.30
C21	-C22	-H22	120.20	C48	-C40	-H40	110.35
C23	-C22	-H22	119.89	C41	-C42	-H42	119.98
C22	-C23	-H23	119.96	C43	-C42	-H42	119.93
C24	-C23	-H23	120.15	C42	-C43	-H43	119.99
C25	-C26	-H26	120.47	C44	-C43	-H43	120.14
C27	-C26	-H26	119.71	C43	-C44	-H44	119.91

C26	-C27	-H27	120.32	C45	-C44	-H44	119.91
C28	-C27	-H27	119.58	C44	-C45	-H45	120.23
C27	-C28	-H28	120.09	C46	-C45	-H45	119.84
C29	-C28	-H28	120.16	C46	-C47	-H47A	110.79
C28	-C29	-H29	120.05	C46	-C47	-H47B	110.83
C30	-C29	-H29	119.95	C48	-C47	-H47A	110.85
Zr1	-C32	-H32	120.69	C48	-C47	-H47B	110.87
C31	-C32	-H32	126.36	H47A	-C47	-H47B	108.87
C33	-C32	-H32	126.14	C49	-C50	-H50	119.90
C33	-C34	-H34	120.12	C51	-C50	-H50	119.98

Table S6 - Bond Angles (Degrees) (continued)
for: s2052a

C50	-C51	-H51	120.14	C61	-C66	-C65	120.0(16)
C52	-C51	-H51	119.88	C61	-C66	-C67	126(2)
C51	-C52	-H52	120.24	C65	-C66	-C67	113.6(17)
C53	-C52	-H52	119.85	C62	-C61	-H61	120.02
C52	-C53	-H53	120.05	C66	-C61	-H61	119.92
C54	-C53	-H53	119.83	C61	-C62	-H62	120.13
C55	-C56	-H56	120.21	C63	-C62	-H62	119.90
C57	-C56	-H56	119.71	C62	-C63	-H63	120.01
C56	-C57	-H57	120.06	C64	-C63	-H63	119.98
C58	-C57	-H57	120.04	C63	-C64	-H64	120.01
C57	-C58	-H58	119.87	C65	-C64	-H64	120.05
C59	-C58	-H58	120.25	C64	-C65	-H65	119.95
C58	-C59	-H59	119.73	C66	-C65	-H65	120.07
C60	-C59	-H59	120.32	C66	-C67	-H67A	109.43
C62	-C61	-C66	120.1(19)	C66	-C67	-H67B	109.48
C61	-C62	-C63	120.0(17)	C66	-C67	-H67C	109.52
C62	-C63	-C64	120.0(18)	H67A	-C67	-H67B	109.49
C63	-C64	-C65	120(2)	H67A	-C67	-H67C	109.35

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    C64     -C65     -C66         120.0(17)    H67B    -C67     -H67C
109.56
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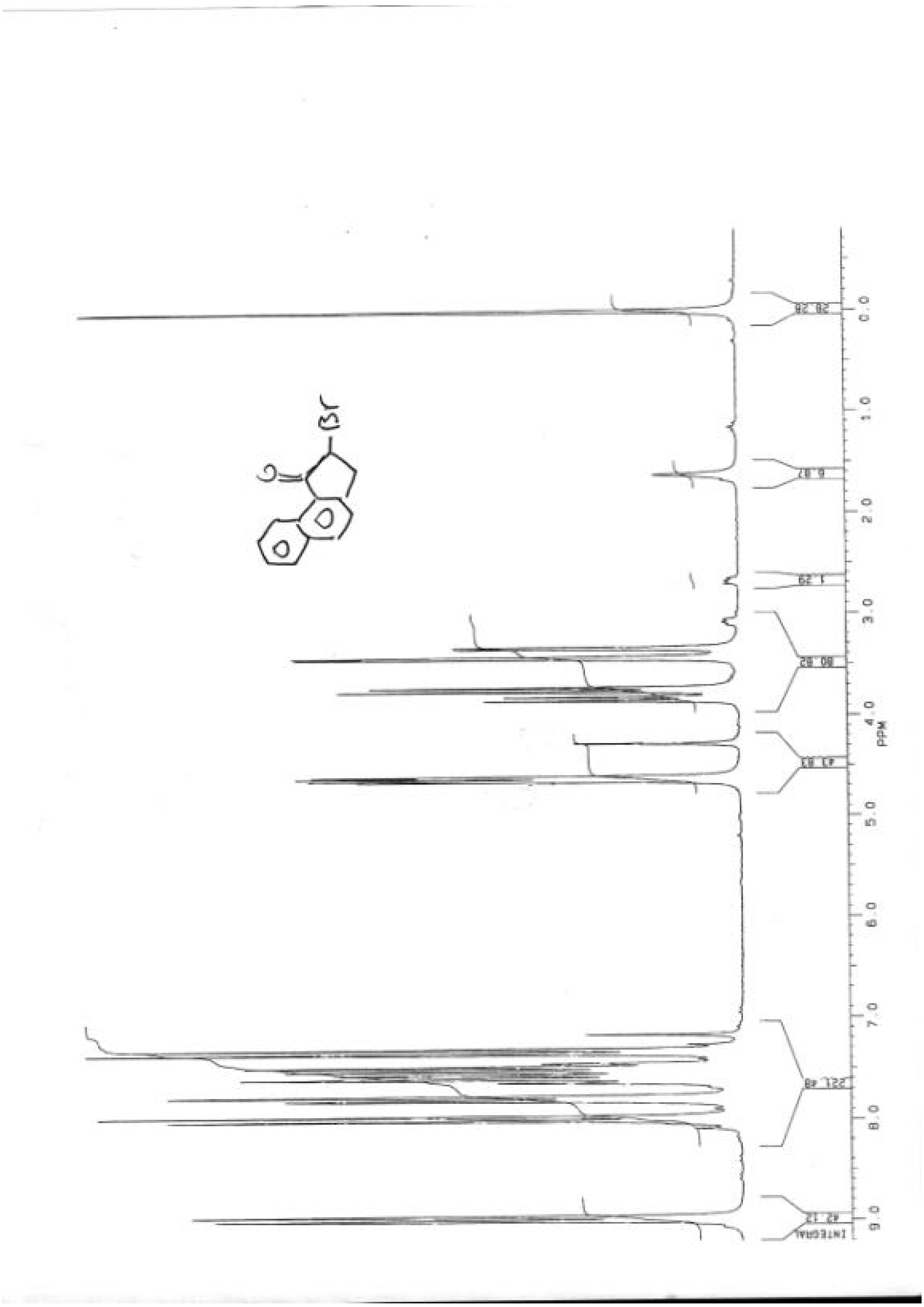
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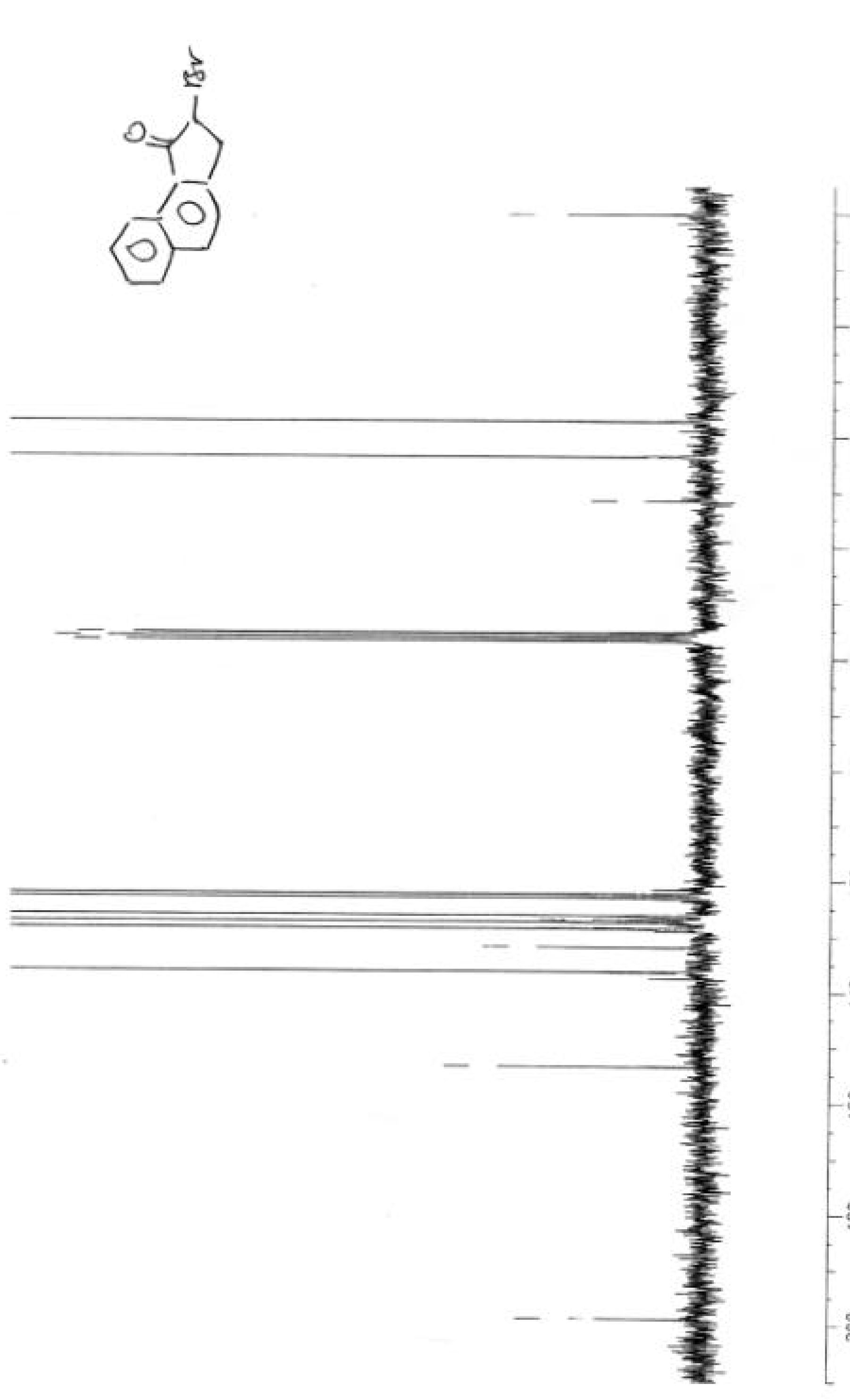
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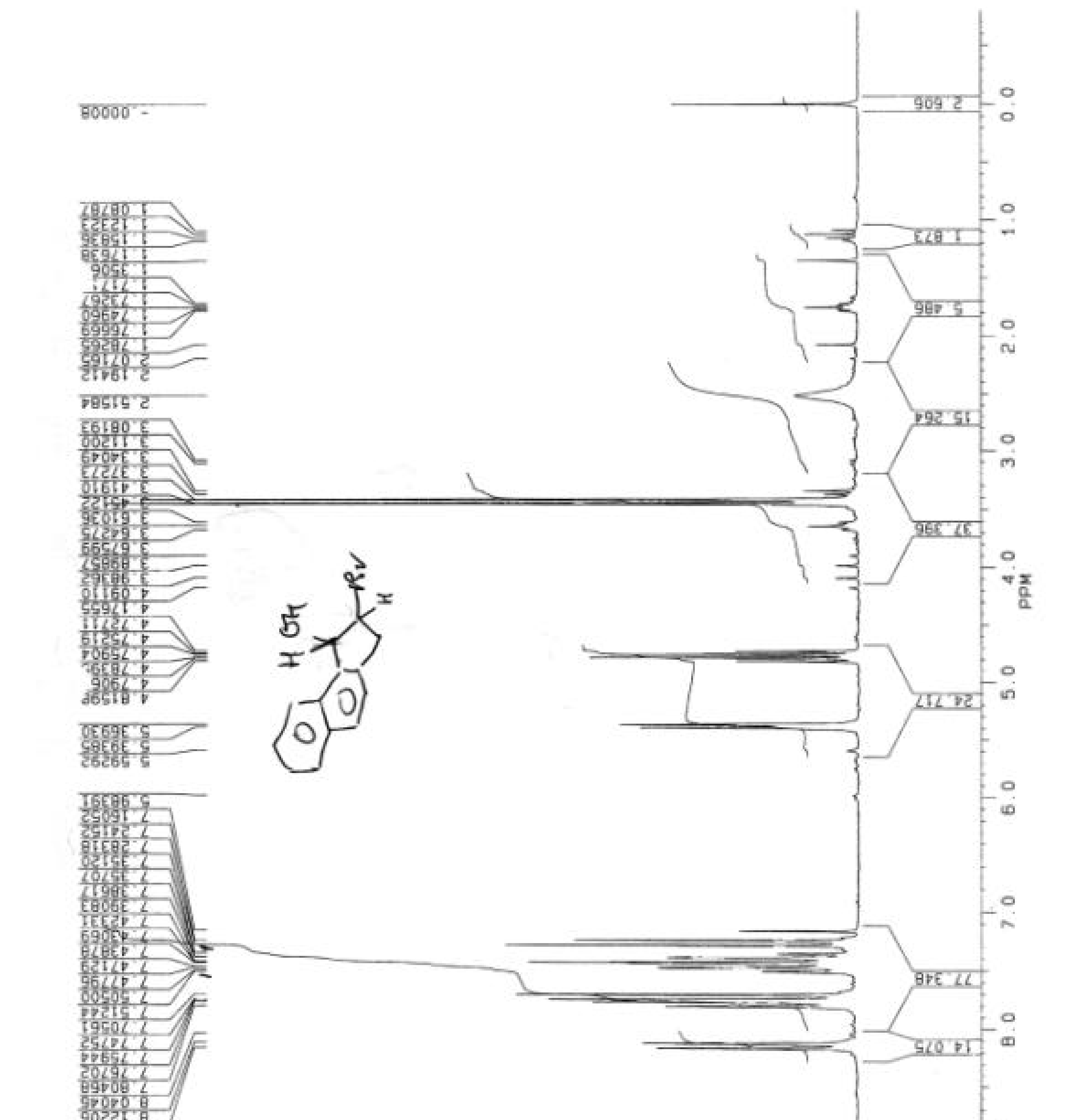
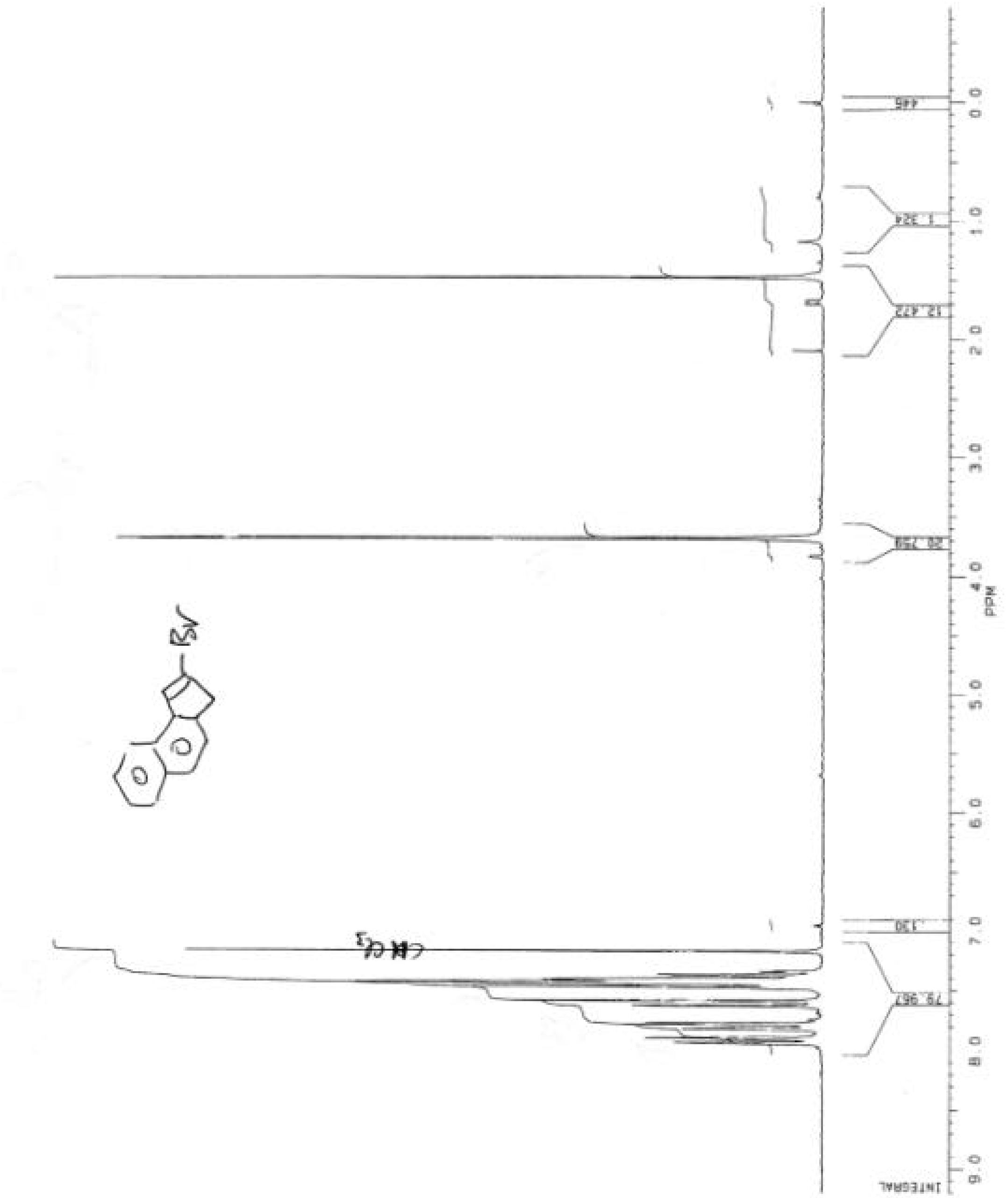
200





CHCl3
INTEGRAL
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12.472
20.759
.130
79.967
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1.0
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4.0
5.0
6.0
7.0
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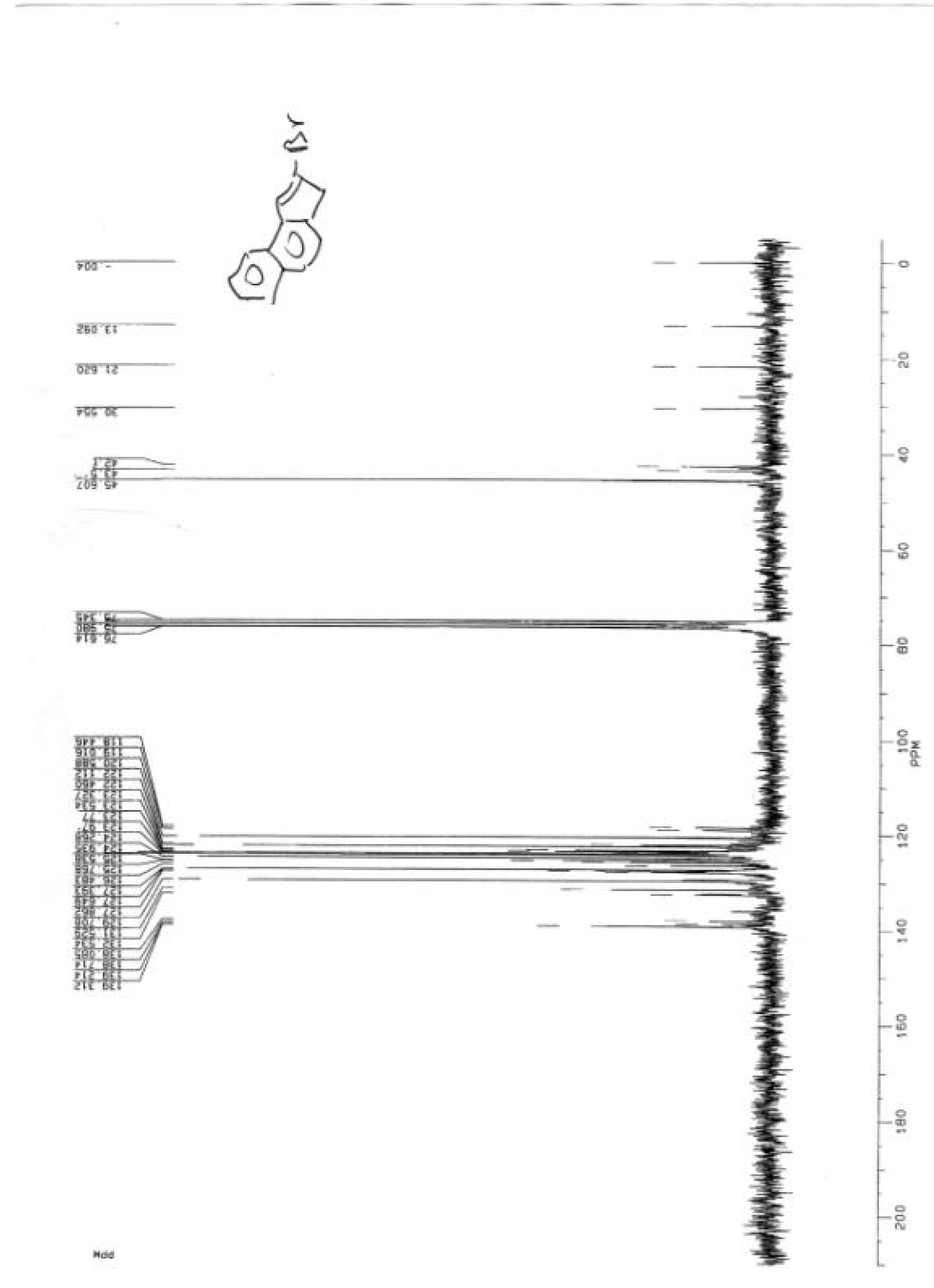
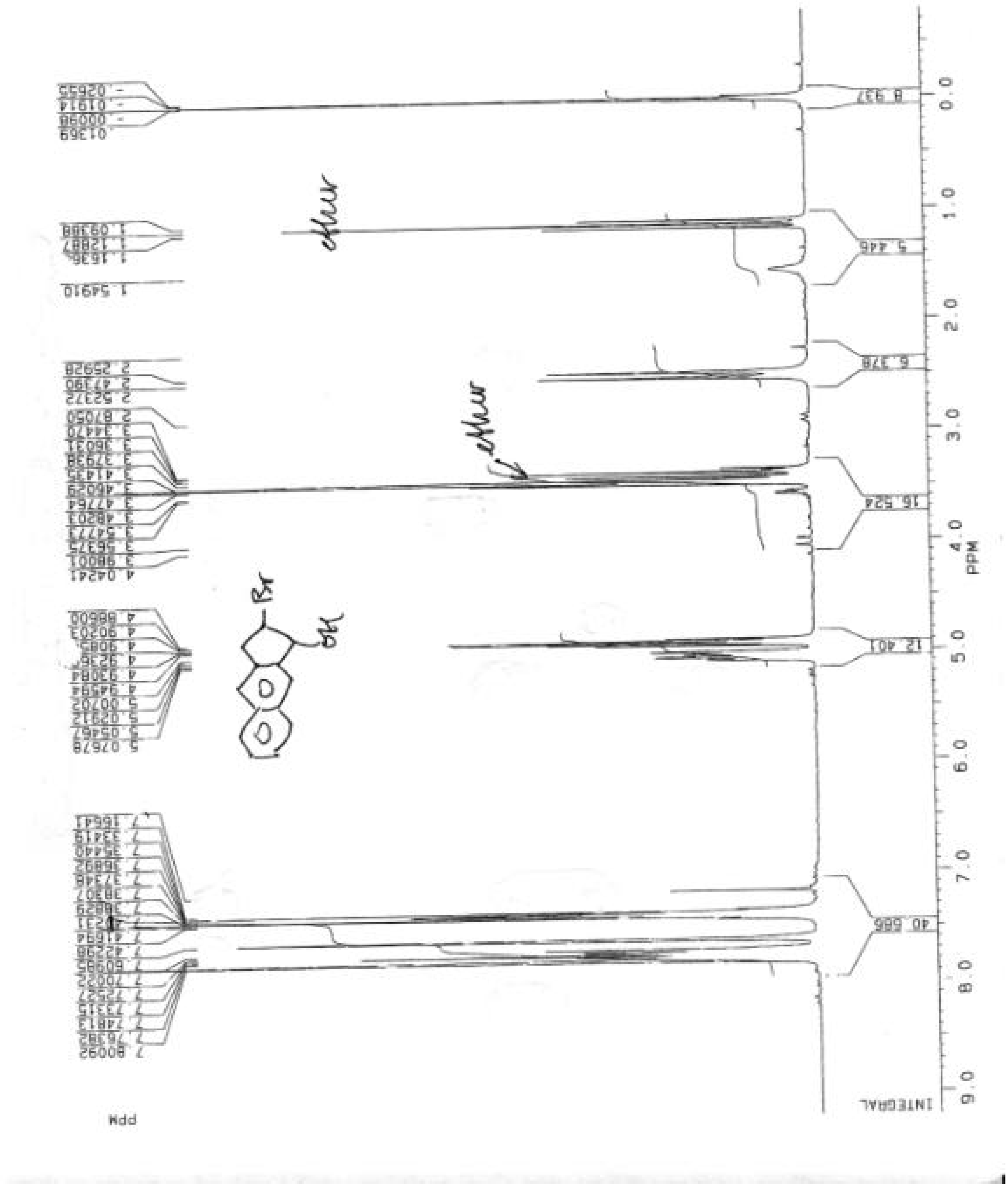
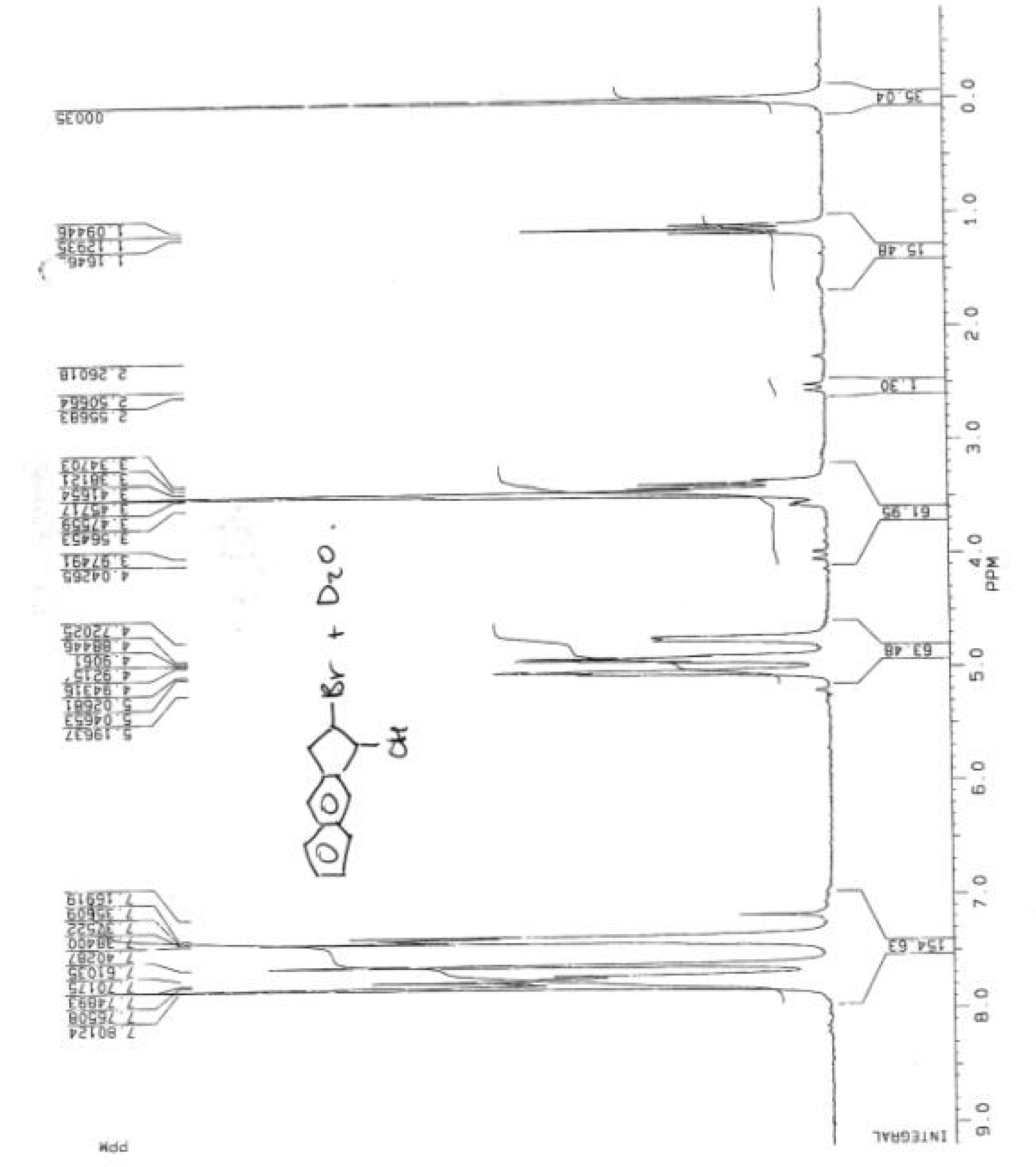
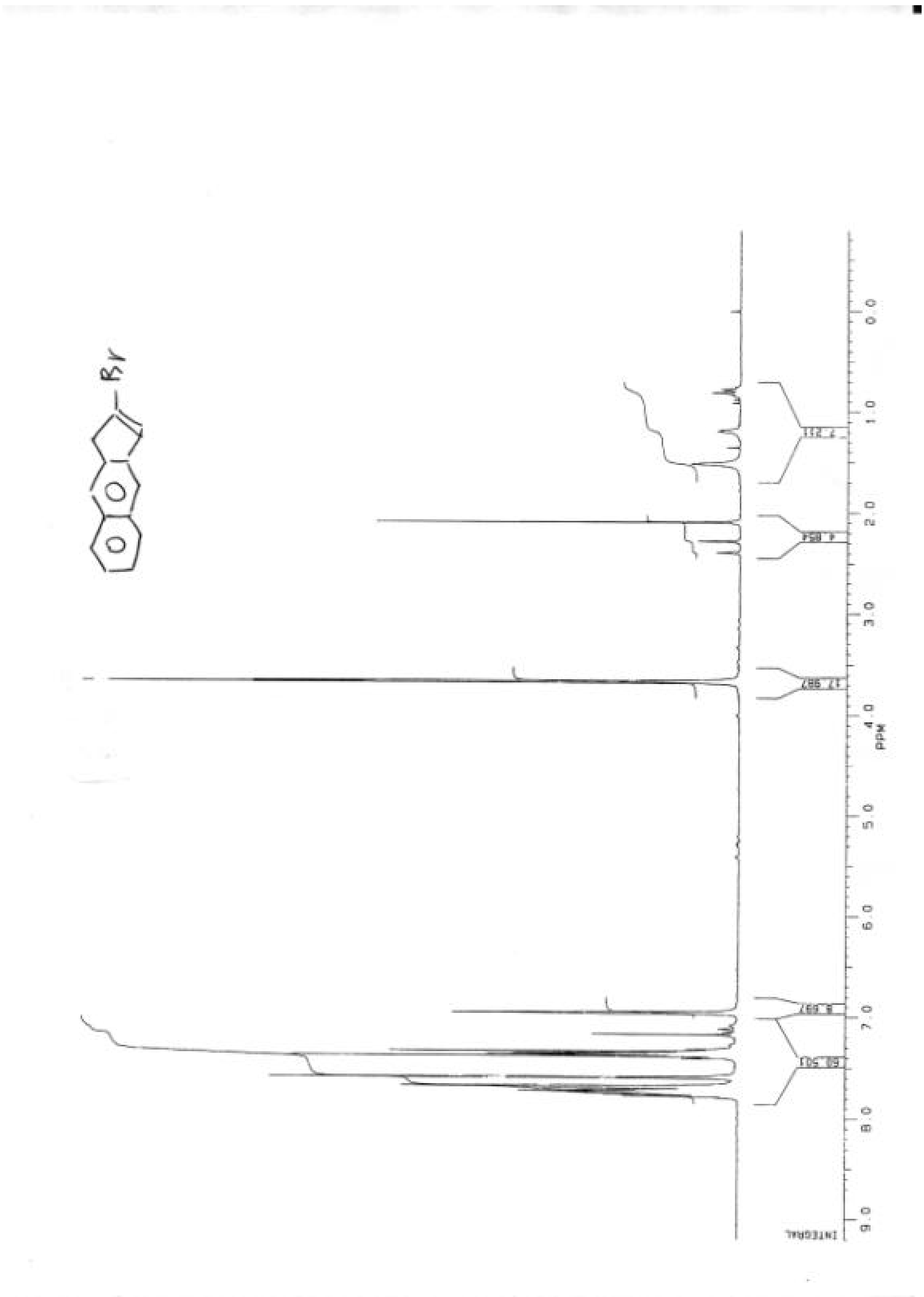
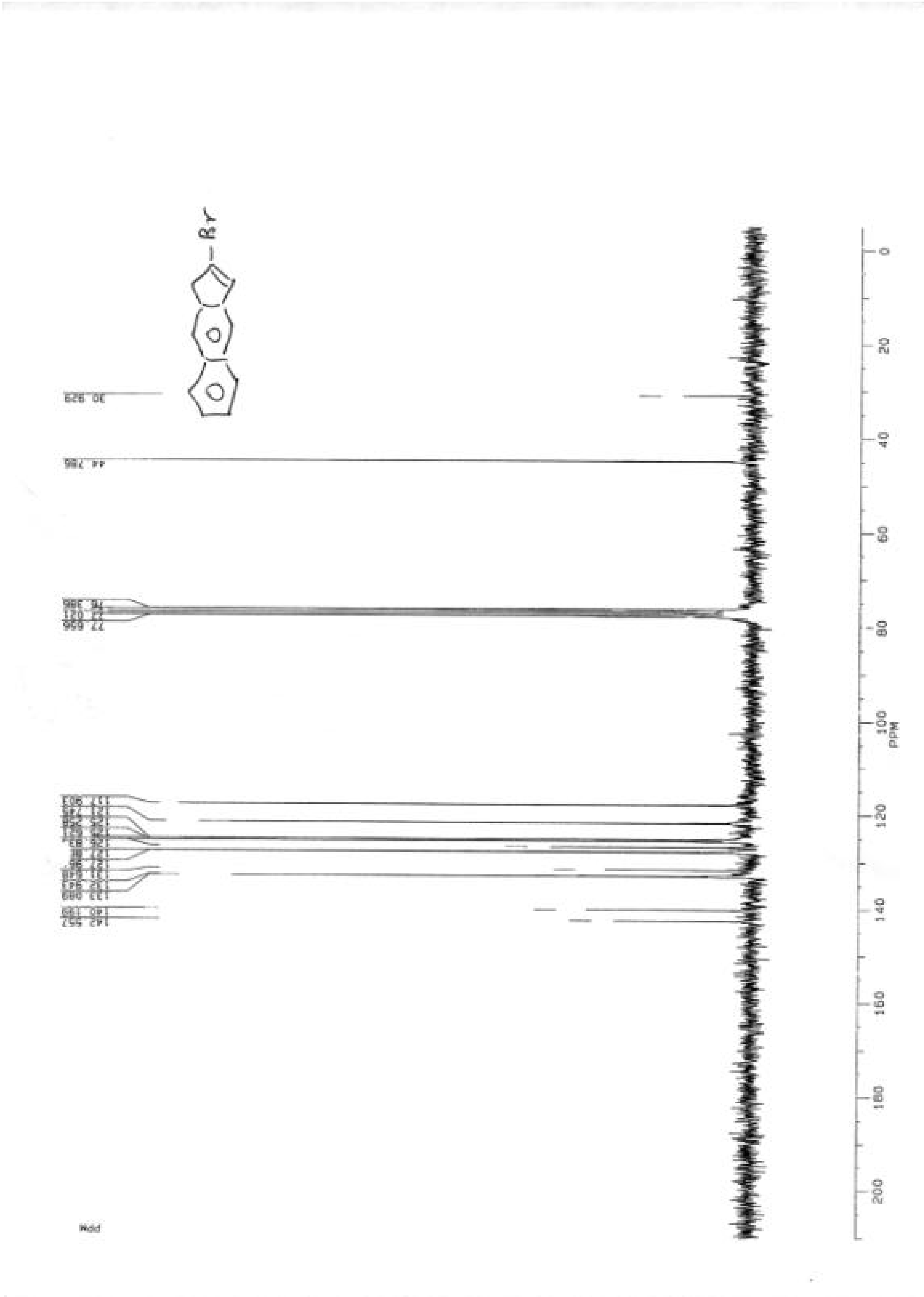
9.0
PPM

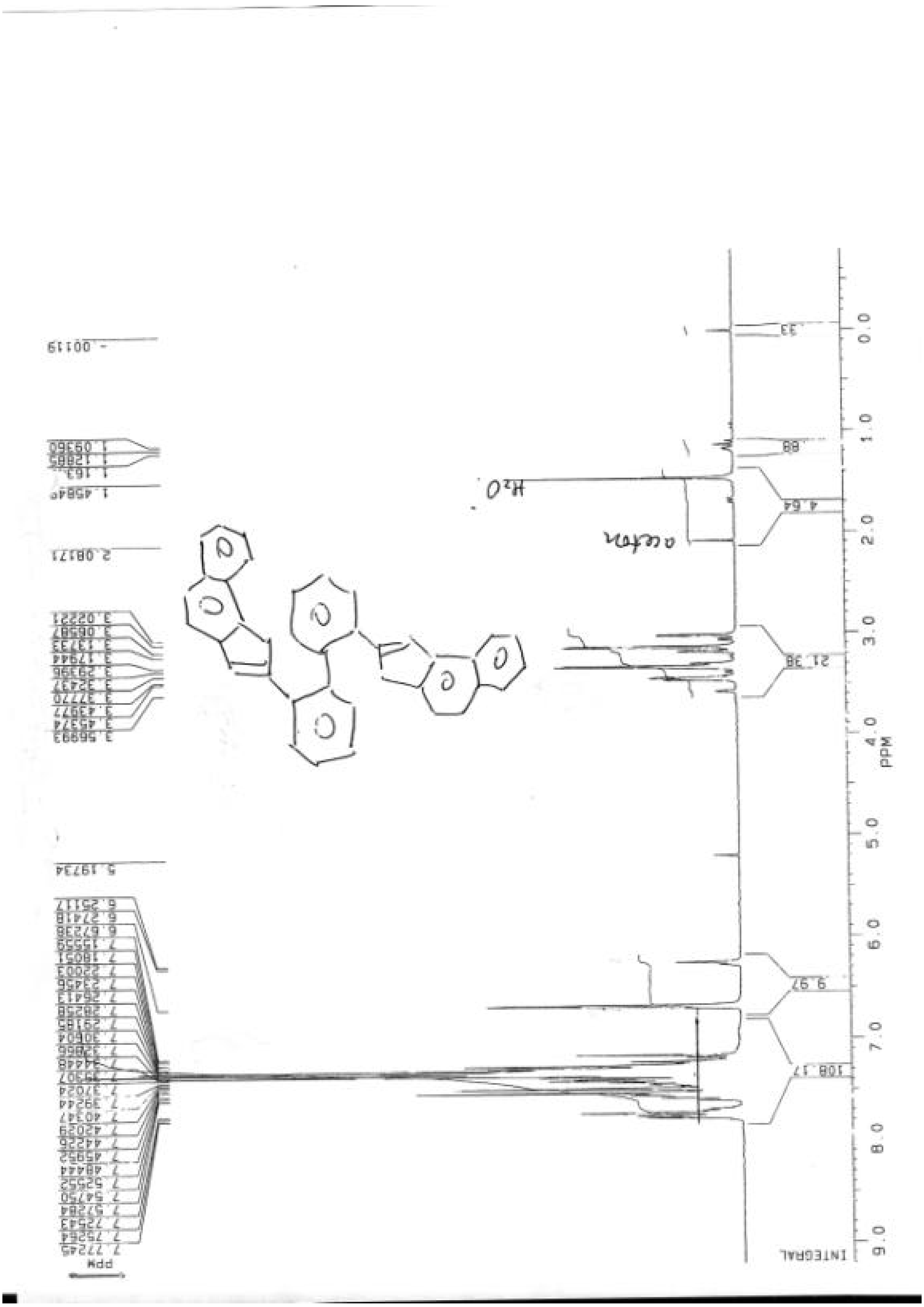


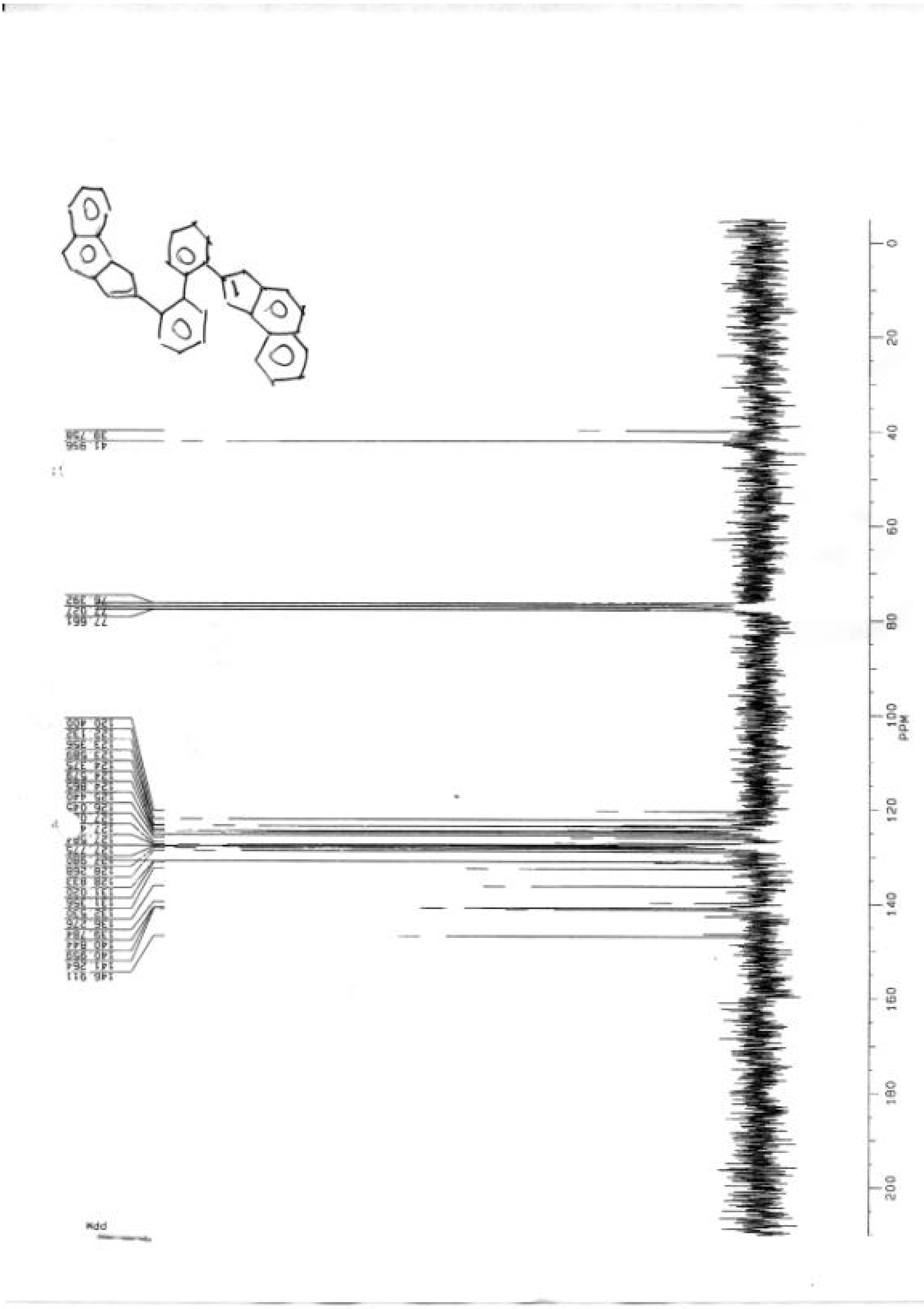


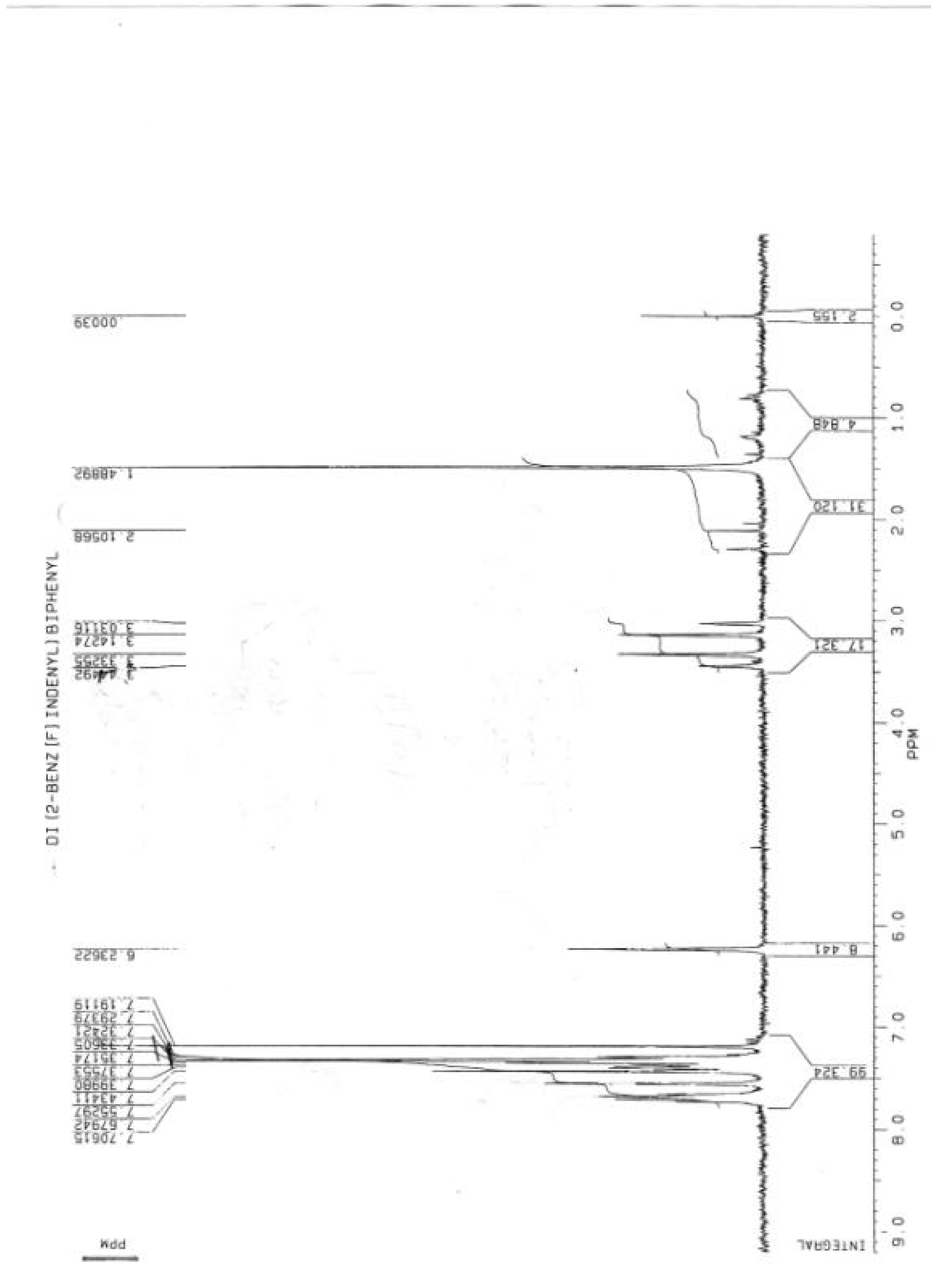


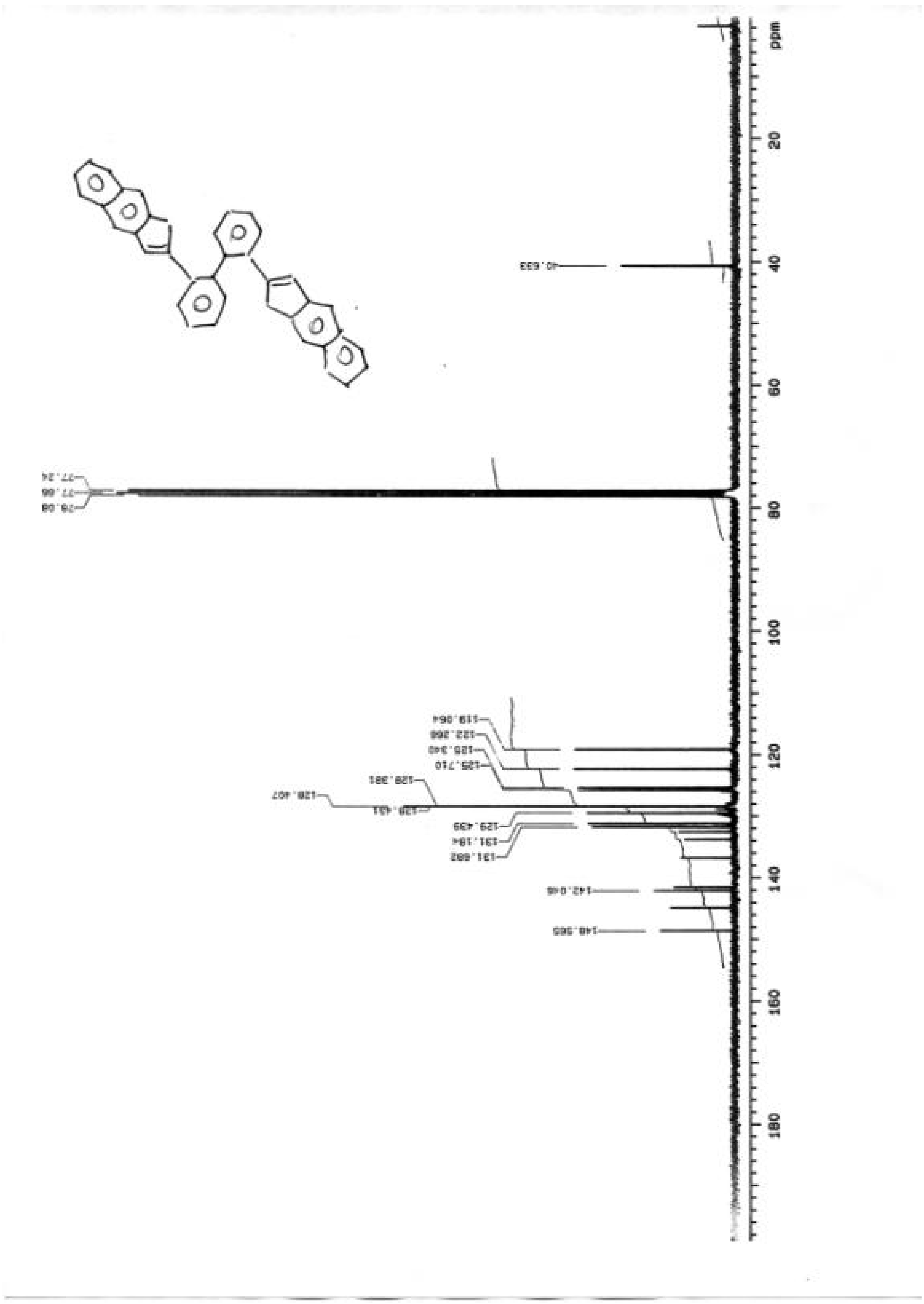









DI(2-BENZ[F]INDENYL)BIPHENYL
PPM
INTEGRAL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77.66
78.08
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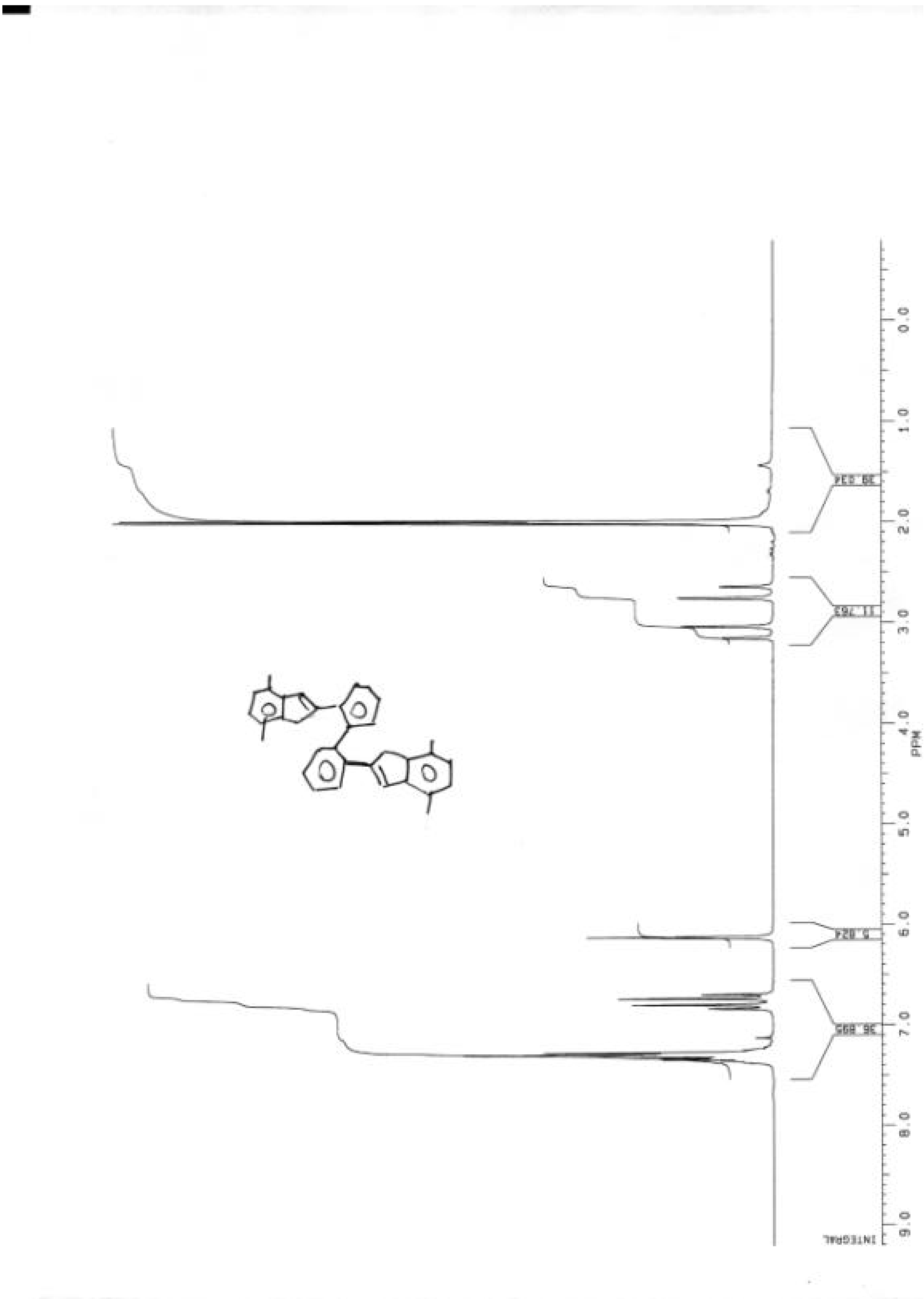
148.565
ppm



0.0
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2.0
3.0
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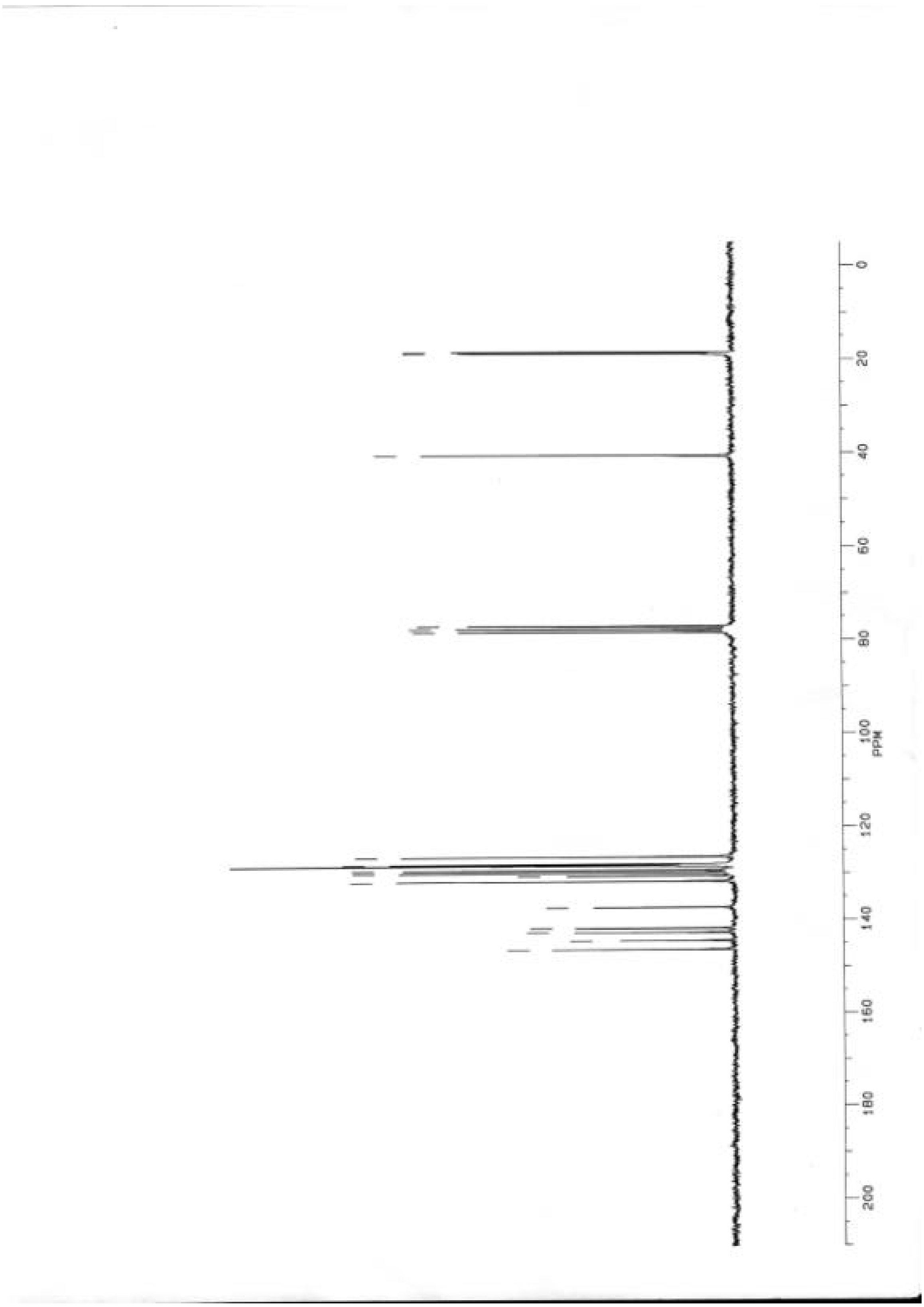
9.0
PPM
INTEGRAL



Reference for the supporting information

[1] Treibs, W. and Schroth, W., *Justus Liebigs Ann. Chem., 639*, **1961**, 204.